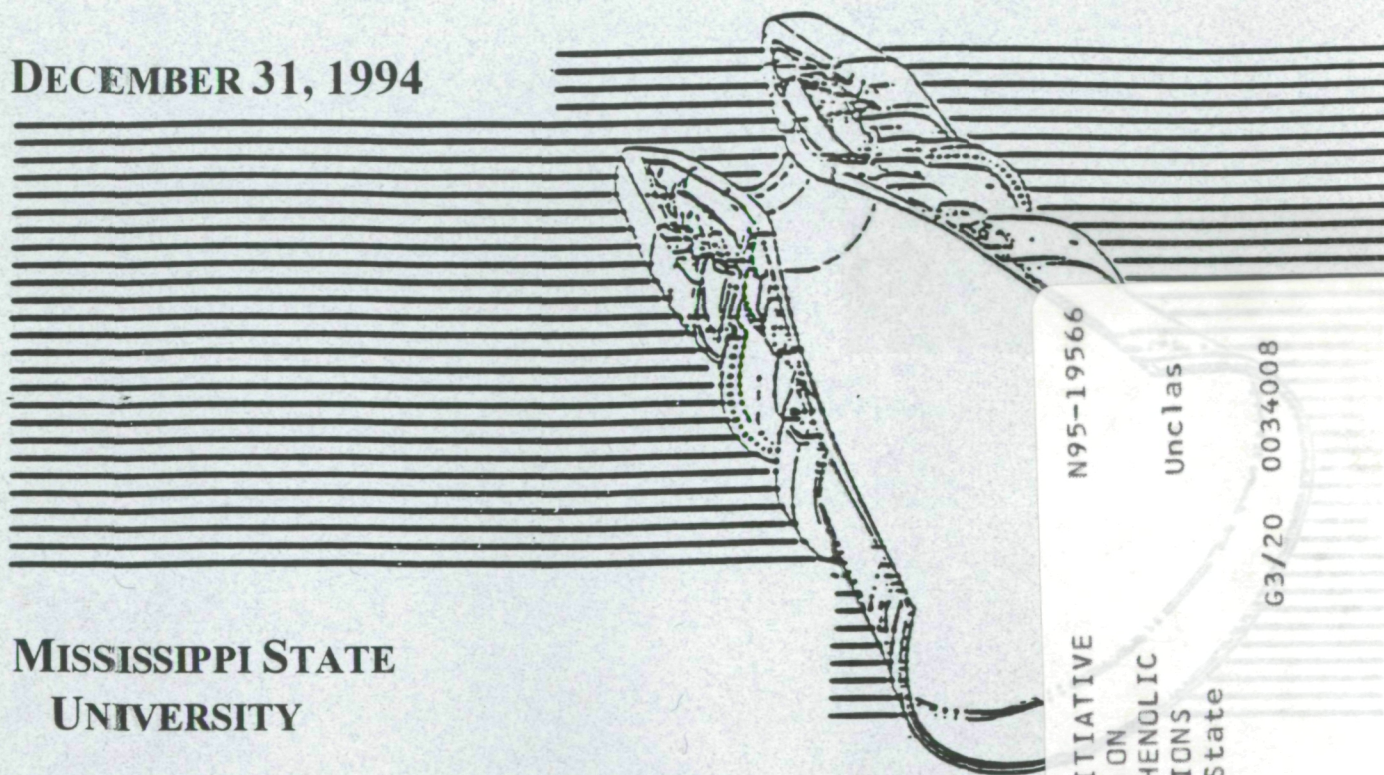# Final Report
Nozzle Initiative Industry Advisory Committee
on Standardization of
Carbon-Phenolic Test Methods and Specifications

Mississippi State University
May 18-20, 1994

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December 31, 1994

Mississippi State
University

NASA Grant NAG8-936

FINAL REPORT
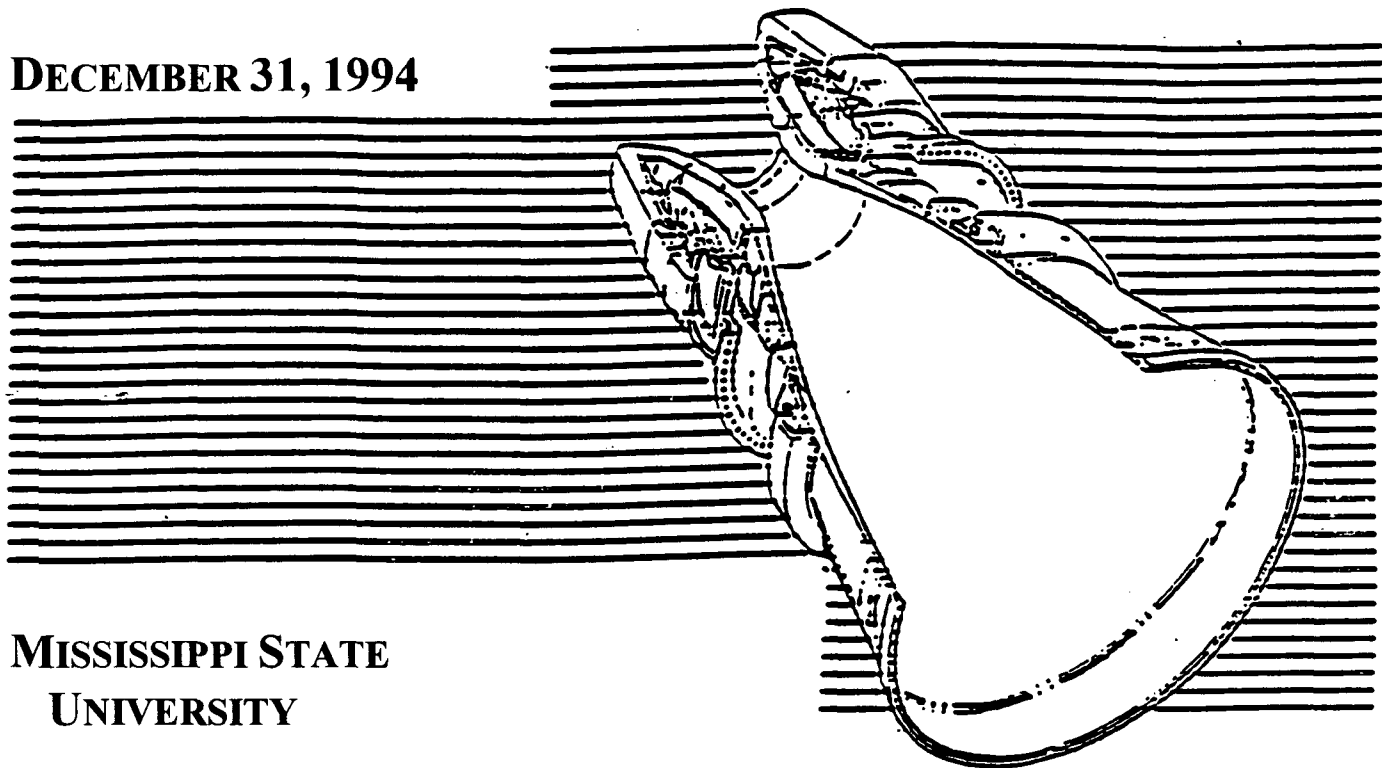# NOZZLE INITIATIVE INDUSTRY ADVISORY COMMITTEE
ON STANDARDIZATION OF
CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS

MISSISSIPPI STATE UNIVERSITY
MAY 18-20, 1994

DECEMBER 31, 1994

**MISSISSIPPI STATE
UNIVERSITY**

FINAL REPORT

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REPORT NUMBER

NAG8-936-3
FINAL REPORT

Notice

FINAL REPORT
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ON STANDARDIZATION OF
CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS

HELD AT

MISSISSIPPI STATE UNIVERSITY
MISSISSIPPI STATE, MISSISSIPPI
MAY 18-20, 1994

COMPILED BY

EXECUTIVE COMMITTEE

WILLIAM B. HALL
MISSISSIPPI STATE UNIVERSITY

PAT C. PINOLI
LOCKHEED RESEARCH AND DEVELOPMENT DIVISION

CINDY G. UPTON
NASA - MARSHALL SPACE FLIGHT CENTER

TONY DAY
THIOKOL SPACE OPERATIONS

KEITH HILL
HERCULES

FRANK STONE
QUALITY DATA ANALYSTS, INC.

DECEMBER 31, 1994

The Industry Advisory Committee

for

Carbon - Phenolic Constituent Test Methodology

is

Constituted under Project 3:2.1.1

of the

Solid Propulsion Integrity Program

(SPIP)

Sponsored by

Marshall Space Flight Center

SPIP-Nozzle Initiative Industry Advisory Committee
Attendees
Mississippi State University
May 18-20, 1994

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SPIP - NOZZLE INITIATIVE ADVISORY COMMITTEE ON CARBON PHENOLIC CONSTITUENT AND COMPOSITE TEST METHODOLOGY
12th Biannual Meeting

Mississippi State University
"M" Club Conference Room
Starkville, Mississippi

AGENDA
Wednesday, May 18, 1994

8:00 am - 8:30 am	Executive Committee Preparation
8:30 am - 8:45 am	Welcome to the Mississippi State University campus - Lynn Chronister, Director of Sponsored Programs - Don Hill, Department Head of Chemical Engineering
8:45 am - 10:15 am	SPIP Overview, Past, Current and Future Activity - Cindy Upton, NASA/MSFC
10:15 am - 10:30 am	Test Methods Manual and Video Tape Library - Bill Hall, Chairman - Pat Pinoli, Lockheed
10:30 am - 11:30 am	Air Force Developed Computer Aided Cure Program and SPC/TQM Experience - Frances Abrams, WL/MLBC
11:30 am - 11:45 am	Magneto-Optical Mapper (MOM), Joint Army/NASA program to assess composite integrity Cindy Upton, NASA/MSFC
11:45 am - 12 noon	Group Photo
12 noon - 1:00 pm	Lunch
1:00 pm - 2:45 pm	Permeability Testing, Round Robin Results - Tony Day, Thiokol - Frank Stone, Quality Data Analysts
2:45 pm - 3:45 pm	Moisture Effusion Testing by Karl Fischer Analysis - Pat Pinoli, Lockheed
3:45 pm - 5:00 pm	Statistical Analysis of Acceptance Test Data - Frank Stone, Quality Data Analysts

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AGENDA
Thursday, May 19, 1994

8:00 am - 8:30 am   Executive Committee Preparation

8:30 am - 9:30 am   NMR Phenolic Resin Advancement
- Cindy Upton, NASA/MSFC
- Tom Fisher, Mississippi State University
- Bob Boudreau, Borden Industrial Resins

9:30 am - 10:30 am   Constituent Testing Highlights on the LDC Optimization Program
- Bob Shaver, Carbospheres
- Pat Pinoli, Lockheed
- Don Beckley, BP Chemicals (Kaiser)

10:30 am - 11:30 am   Carbon Sulfur Study, Performance Related Testing
- Tony Day, Thiokol
- Pat Pinoli, Lockheed
- Bob Looney, North American Rayon (NAR)

11:30 am - 12 noon   Current Rayon Specifications and Future Availability
- Bob Looney, North American Rayon (NAR)

12 noon - 1:00 pm   Lunch

1:00 pm - 1:30 pm   RSRM/SPC Implementation
- Tom Paral, Polycarbon
- Jim Thomas, Consultant
- Jon Weisphenning, Fiberite

1:30 pm - 2:00 pm   SRM Test Methods, Delta/Titan/FBM/RSRM
- Keith Hill, Hercules
- Tony Day, Thiokol

2:00 pm - 3:00 pm   Open Forum on Performance Based Acceptance Testing - Industry Experience
- Cindy Upton, NASA/MSFC
- Gary Brown, Aerojet
- Tony Day, Thiokol

3:00 pm - 5:00 pm   NMR and Engineering Laboratory Tour

Chronister	Welcome to MSU and I understand from talking to many of you that this is your first visit to Mississippi State. I hope you have a chance to see the campus. Is that built into your agenda at all? There are a number of things that you need to see on campus and things that we are proud of. You really need to go to the Cheese Shop and take home some cheese and help the Mississippi State economy.

I have been here just a couple of years and absolutely fell in love with Mississippi State University and they told me there were a lot of benefits to working at MSU. One of the real benefits that I have is getting to talk to groups like yours and welcome them to our campus. Dr. Ralph Powe, who is our Vice President for Research would be here, except that he is Washington. He is head of the national committee for a program called EPSCoR, which is a program benfitting 18 states that stimulates cooperative research.

One thing that I thought of when I looked at your committee composition was the wonderful interaction, federal laboratories, university research, and industry and if you look back for, say 10 years ago, this was more unique than it is now. You will see, especially at the federal level, a need for partnership, collaboration. I have been in research administration for more than 20 years, and when I think back 20 years, you would see the faculty doing research serially, doing a little bit and then building on it. In some instances, you might have parallel research going on at different laboratories. Seldom was there interaction. I think this particular group should feel very proud of what you have put together.

Since only three of you have ever been here before, I thought you might like a little information on the university. MSU is over 100 years old and was established as a land grant university. We have gone through a few name changes. If you look at the research programs and teaching programs, and the service programs, the focus is mostly agricultural and engineering. We have approximately 15,000 students with about 14,000 actually on campus. We also have a Meridian campus and we teach some courses at the Stennis Space Center on the Gulf Coast and two other off-site areas. Last year we did a little under $60 million in extra mural programs, such as research, educational, public service and scholarship programs. Of that $60 million, NASA accounted for about 42 awards for a little over $2 million, and looking over this list of companies that you all work for, we also have a number of contracts with your companies as well. This project of Dr. Hall's is the longest running project in the history of the Chemical Engineering department.

I hope you all are touring the NMR laboratory. I think that once that lab gets fully operational, it will be one of the most impressive NMR laboratories in the South. The instrumentation is phenomenal. If you have any questions about Mississippi State University I would be happy to answer them. This is just sort of a quick overview of who we are and what we are.

Pinoli   Thank you, Lynne.
              Cindy, do you want to start things off?

Upton   A lot is going on in SPIP right now and I thought that it would be a good idea if I gave you a program overview of where we are now and what is coming down the pike very soon so that we can see where we have been and what is ahead of us. As the NASA lead for this group, I have had a lot of visibility to the people at headquarters and people at Marshall in the SPIP program office about basically what they expect of us. I am calling this group at Marshall and asked that the people who are giving us proposals for the new NRA to call us the Ablative Materials Test Methodology Development Committee because that encompasses everything in the area of testing for composite materials in nozzles. We are responsible for test method development for everything in solid rocket motor nozzles from the constituent all the way through the cured composite, everything in between.

There are two things that headquarters is asking us to do. They have stressed this to the point that they are really not interested in anything else. The first is the development and implementation of performance based acceptance tests. Now a lot of people get really nervous about this because they say that this has not been done in the past, it may not be able to be done, and believe me, through the managers, I am telling them that I make no promises. We will *try* to develop tests which do indicate performance. Don't get too nervous about that. I am not making promises for us. I am just telling them what we plan to do.

Another thing that they want us to concentrate on is a measure of improvement. In other words, if we improve, say the density test, then give us a percentage that the test is better. Now that is very

difficult to do because a lot of times the new test is orange to the old test apple and you can't really compare them and sometimes when you do co pare them, it is really difficult to get that numerical measure of improvement. This is one area where Frank Stone and his new company will be very useful to us. He is already looking at some of our old data and seeing where improvements are being made and trying to quantitate improvements for us. Those are our two main goals, performance based testing and measurement of improvement.

Another thing that we are starting to do in our report is coming up with our own specific nomenclature for what we do. These are some terms that the SPIP program office and I developed so that when we publish reports and documents, we are consistent in how we describe a test. You can see from your handouts that we have basically three types of tests.

I have wanted to share with you pretty much where we are. That final test, we had planned to work with Thiokol and others and reach a final test by the end of this year. These Thiokol in plane technical directives, we should come out v a test that we can perform on tag ends or whatever we want to do by the end of the year. Now on this test the instrumentation is so different from place to place, we will be coming up with test methods for each place that uses DSC and we are calling this a standardized test. Carbon assay testing is an old test. We really haven't worked that for a long time. Pat is going to write a standardized report. BP did a lot of work on this, Marshall, Lockheed, and Tom Paral did a lot of work on this. We have to write it up and put it in the test

methods manual and be done with it. We will probably do a video tape on that one too. Then Karl Fischer testing, we should soon have a standardized test report. Permeability testing, probably Tony can come up with a standardized test plan just from the round robin that he has. I think we are very close on this one. You'll hear about that during his presentation. The high temperature testing, we expect to have some data soon, and then we can determine how meaningful that is going to be for us. Tom has received a solid probe for his NMR and you will be touring the NMR tomorrow afternoon and he has begun work on the solids. He will be discussing that at this meeting.

This is the last year of SPIP as it is now. We need to close out everything and we need to understand our deliverables for this year. At the end of this year, which will be December 1994, we will basically shut down. We will get started back up, but it will be different when we start back up. Tom will present a final report on the NMR work that he has done to date. An interesting side note, a lot of people don't realize all the work that Tom has done in NMR, because when he stands up here and talks, he gives you the information that he was planning to get, but he doesn't necessarily tell you all that he has had to do to get that information. Now, the fact that he is writing a final report in now way means that we are finished with NMR. Basically he is laying the groundwork so that we can use NMR as a part of our program. Tom is almost there. He is adding the last section, solids to our game plan, but he is not going to be finished with NMR.

HPLC, we do expect to have a standardized test out by the end of the year. We have doing a lot of work on it at Marshall and we have been having equipment problems so that may get delayed. This is being requested to replace an existing test that does not correctly monitor the change in molecular weight. This is something that we are very close to and we hope to have it something this year.

Magneto-optical mapping is something that I am going to talk about later on this morning. This is something that Army is working and they have given me their charts. This something new and they want to see how well this will work on our materials. I am going to attempt to explain this to you, but I don't fully understand it yet, myself. By the next meeting I hope to have one of the Army guys tell you about it or understand it better myself and have data to show you. This holds some promise and this is something that is no cost to us.

The density test, that was the change in displacement fluid, and Pat feels like that is a simple thing to wrap up. One good thing about closing out, is it is forcing us to do a lot of house cleaning. There are so many topics on our agenda and we get just so far in a test plan and we don't really get to finish it out. That is really bad, because when I go to the big SPIP program meetings, a lot of times people are criticizing SPIP because they say that as a whole the program does not carry things through. There are a lot of things that we had finished, but we hadn't really gone out and sold them.

We are going to do that. I don't this group to be accused of dropping the ball.

Chemometrics is something that Frank Stone and company are doing. This is Frank's first year on board with us. He has attending other meetings but only as a guest speaker. Frank has been some work along the way and he will submit a report at the end of the year also, but again this doesn't imply that we are finished with chemometrics. There is a lot that Frank can do to help our group.

In March there was a big meeting at Marshall and it was industry representatives, managers of the programs, the SPIP people at Marshall and some headquarters people and out of this meeting came a road map for the remainder of the SPIP program. We prioritized all the work packages and basically talked about our funding situation and what we were going to be needing. This group is the number one priority in SPIP and I was very proud of that, but one of the reasons that we are number one is because even though I have told managers that I am not promising anything, they expect us to come up with performance-based acceptance tests. I was very up front with them in saying that I offered no promises. Another thing that helped us become number one is that traditionally in this group, industry has been so supportive. I really appreciate this and it has all paid off. We have been promised a very generous budget for next year.

Now this right here is Corky Clinton's solid TQM team and they are prioritized number two. The large scale certs which is solid

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rocket combustion simulator is a new program and it is nipping at our heels. It is being sponsored out of Marshall and has a great deal of political clout behind it. It is very controversial because there are a lot of people who don't want this program. This is going to be a problem because they are after our money.

Number four is the bondlines and they have been pushed down in the program and one of the reasons is they are being accused of being a hobby shop. That is a group that is doing work for the sake of doing work, like a science project. There is no real implementation plan, no real customer. I don't think that we have a problem with being called a hobby shop because we are looking toward implementation. I don't really know this technique, but it is an ultraviolet fluorescent technique.

The next is a materials database which feeds into the structural code under 3.1 and those two are tied together and you can't have one without the other.

Thomas   Cindy, what does the budget look like for next year?

Upton   Overall on SPIP, it is down. They are expecting somewhere $10-12 million and that depends on how you count the $2.9 million carry over that we did not get this year. I have been promised over a million next year. We don't really have a clear picture of our funding for next year, so that we when we go to evaluate the NRA for this year, you don't know what to pick and choose because something could be cut. I have been asking everyone to overdo it

and I will sort it out as best I can. It is a real mess and that is a good lead in on the NRA.

Next week I will be evaluating the proposals that have come in and there are basically two procurement cycles, but everyone, I think, has pretty much taken the first one. For the first one, the proposals are due Friday and we start evaluating Monday and they are expecting to award the contracts October to December. I am very nervous about this because I think our group is great the way it is and I like the way that we do business. This leaves the barn door open so to speak to people who are nipping at our heels. Basically what SPIP is trying to accomplish through this NRA is a way to give industry a chance. SPIP has been going on since 1985 and there is some concern that we need to regroup and hit it again and make sure the needs of the programs are being met. Ostensibly, that is a fine goal, but it is going to be messy to get there. The idea of the NRA is, rather than request proposal where we tell industry what we want and we receive proposals back, this way we just say this is a solid rocket nozzle and what are you going to do about it. They send these proposals in and it can be exactly what doing now or it can be something totally different. There are three basic areas that SPIP is pushing for the proposals to meet. They are basically saying that if these three criteria are not met, then the proposal will not be considered very strongly. That leaves you with the problem that if you have a company that you really want to work with but whoever wrote the proposal seemed to get lost. Another important factor for SPIP is national outcome, not how it affects one particular program, but America. No pressure. What does your work mean nationally. Again, I am not really sure what they are

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looking for here because there are a lot of things that we can do, but I don't really know about national outcome.

This is a big, big thing this time, cost sharing. They want some kind of contribution from the proposing company. I have put together charts on it that will show the return on SPIP dollars from you. You have been so generous in volunteering your time to come to these meetings, giving us resources, running tests for free in a round robin series, or evaluating something for free. We guestimated a cost and we figured out a ratio on returned dollars and at one time it was 600 to 1 returned dollars. That was back in the days when were hardly getting any budget. Over the years as the aerospace industry shrunk, we have not been able to get quite that kind of ratio, but it has always been at least 8 to 1. The SPIP office has been very impressed with this. However, these charts have been shown to other people and they will generate charts and they will submit the same kind of information on an NRA and now the NRA people are expecting this cost sharing to be addressed.

The third and probably most important consideration on these NRAs is the implementation. Again, hobby shop is the latest buzzword. What the SPIP office told me was that no matter how good a proposal might sound, if there is not a way to get it on the street, they don't want it. Yellowcreek is our big window of opportunity. We can say that the test plans that we are working on now will be ready for implementation into the nozzle facility at Yellowcreek. I don't feel like we have a problem with implementation.

This group is scheduled for a close out report in the first quarter of FY97, so really we have FY95 and FY96 to do our real work. When I submit a budget, I always go ahead and submit a budget for the full 97 year, because you never know. Things change so much at headquarters that you never know.

That is basically what I know. Are there any questions, over? I do have one more thing for you. Part of what brought all this about was last summer a peer review team was formed because SPIP had been going on for quite some time and on the review team was Buzz Wells, who as you all know is associated with the Air Force. I was at this meeting and Buzz Wells was talking about the goals of SPIP and he questioned how many had read Dr. R. P. Feynman's report on reliability and shuttle report. No one raised their hand and he commented that no one should be working on flight hardware without reading this report. I went to the NASA library and there is a big Challenger report. There are volumes and volumes and it covers the proceedings and everything. I fished out of that the Personal Observations on Reliability of Shuttle. I have made copies for you. I found it very enlightening. If there are no questions, I am finished.

Thomas   Cindy, what was your nozzle budget for 94?

Upton   I don't know what Hercules got. I got around $400K. Keith, do you know?

Hill   I could take a guess, and say something like $7.9 million.

Upton	I got about half of what I was promised.
Pinoli	Bill and I put an item on the agenda about the test methods manual and the video tape library. I think we did it in recognition of the fact that we wanted you know they are being carried out. The test methods manual that Bill and I have worked on has been kept up to date and the changes that we thought were appropriate have been added. As we have gone through, we have worked those specifications to a point where we feel satisfied with them. I was just talking to Bill about the possibility that we might expand it and put in some of the pitfalls that we have gone through.

The video tape library, we did put out one tape on carbon oxidation testing. Along those lines, I might mention to the vendors that in the future, we may ask to visit your facility and tape some background information for use in the video tape library. When you get into this business, you find the people that do this like to travel, and it does strengthen any video tape if you show the real manufacturing capability and what is going on and why you are doing these tests. For the carbon oxidation test, we picked up some real good background footage at Polycarbon.

One question that we have wrestled with is whether the tape should be a step-by-step procedure or an overview tool that will give a feel for what you are trying to do. Through Corky, we have received a directive that Marshall would appreciate the very step-by-step procedure, so that it could be a film that you would give to a technician. That is the way the Karl Fischer testing is done. Are

there any questions before we put Frances up and give her an opportunity to tell us about everything that she has been doing?

Abrams   I wonder how many of you have read my report on the 84 anomalies. It was sent to NASA. I wouldn't say it is the best piece of work I have ever done, but I think that some of the problems that I identified at that time are still a problem. I think that those are some of the problems that John Koenig began to identify in the next year or two are still problems. I think perhaps a review of my past history would be beneficial.

I am a manufacturing person, or a processing person, and I have worked both sides of the house. Though most of my work has been in carbon-carbon, you have to do a little carbon-phenolic along the way, and during the last few years I have been studying carbon-phenolic fairly heavily and doing some work with it. What I am going to show you today is sort of a full gamut of what we have been doing in processing and curing at the Air Force. It includes an awful lot of different areas so I am going to start off with some background material which may or may not be interesting, but if you bear with me, I think it is important.

The first one is my definition of intelligent materials processing. I am very encouraged to see that you guys are working on acceptance tests. It is my opinion that one cannot do intelligent processing unless you know where you are going. That means you have to know what kind of physical and mechanical properties, thermal properties, whatever is important in the material, are necessary to perform the designed job that it has to do. That means that

processing has to coordinate with mechanics, coordinate with quality control and it has to be used by those people as well.

The other thing that the Air Force is getting a lot of attention about is efficiency. In our industry, we don't just burn things up. In our industry things stick around on airplanes a lot longer than we expected and so we have to be concerned about life cycle costs, maintenance costs. Even disposal, now, is becoming a critical item.

There are two actual phases to manufacturing, the development phase where you make the parts, and the second is the production phase. The reason that I make this point is because when you talk about making something, a lot of the Air Force work is aimed at making one attempt. With large and expensive parts, we have to do it right the first time. This limits our use of some techniques. In order to lower the overall cost, you need to find inexpensive methods and to increase our slope so that we can learn faster in that development phase.

As you can see in this example, in the 250 production the recurring costs are the largest part of the equation. That is what makes the development phase so important and to do it right the first time.

There are a couple of ways to go about processing. You are going from some raw material, which we hope you know something about, to some required form. There are a number of ways to get there. The optimum process is not necessarily a straight line. A lot of process don't have this intermediate step. You make the material at the same time that you make the part. There is a lot of value

added in that kind of process. This is kind of process where you make the material first and then you machine something out of it, or you stamp it, or mold it.

What we have done in the materials area is come up with a variety of tools for processing. We may not cover all of the possible applications. the point of this is that none of these tools is the end all for everything. You have to have someone with intelligence to choose these tools, to use these tools, maintain these tools, and to discard them if they are not doing the job.

How do we do this really? We do it by trial and error. A lot of people knock trial and error, including me, but it has made an awful lot of good parts and we are flying planes, and have made composite parts that have been developed by trial and error. Someone had done something before that took that something and when modified slightly came up with some kind of plan. The lesson in here is that you don't learn anything from "the good". You only increase your experience with a bad experience. We have increased our experience a lot.

If you think design of experiments is new, I have a report that was written in 1963 that outlined a design of experiments to develop cure cycle in testing new materials. It has been around a long time. People haven't used this a lot. It means you have to think a little bit about the possible variation and what they might be and then you have to select them intelligently because you can handle all of them, especially in a complex process. You have to be able to quantify your variables. One of things that has always bothered me about

this is that if something is not working exactly right, it really hard to pinpoint what is wrong and you don't know where you are. One example of where I have used design of experiments is in the bagging. This is something that got a lot of attention. The bagging had a very critical affect and I think one of the things that I identified in the 84 report is the way Thiokol was doing their batching. They were compacting, a little like taking a telephone pole and pushing in on it.

Statistical process control, I don't have a lot of experience with, but I have talked to a lot of companies that are using this. It is really good if you can afford to throw away that many parts. Generally the parts that we are talking about have so much value added that what it is really good for is keeping track of what has gone on historically. You never really know what you are going to find. One of the things that impressed me in 1984 was the lack of records. Clearly the Air Force does not have enough parts to make full use of statistical process control and we can't afford to wait until we find our 500 parts are good, but tracking product quality is something that is very critical.

There has been some resistance to using some of these methods to bringing improvement in. We put together what it costs to qualify a new materials in a part and the sum absolutely floored me, so you can understand the reluctance in bringing improvement in. There has to be method for bringing improvement in or we just don't have it.

This is a Navy example, so I can talk about. This is an actual case where they were making a part at a company which will be nameless and they had thermocouples on the part used to follow the cure cycle. They decided that they were rejecting a lot of parts because the cure cycle was out of spec and so someone in the program office decided the way to solve it was to remove the thermocouples.

To get back to the diagram, when you start looking at what you actually have to control and what you want to get out of the cure process, in any kind of polymeric composite. You actually have control over very few local boundaries and through those you have to manipulate, sort of like trimming limbs with a tall pole. It is a balancing act. You can't manipulate the things that you really want to manipulate, which are the physical properties. If you can have control over them, then you can have control over the mechanical properties. The problem is that if you look at what happens when you try to figure out what these things are doing to these things. It is really more like balancing on a rope. It is difficult to predict, let alone control. It is not difficult to predict qualitatively what kind of influence these different things will have on it. Each of the techniques has its weaknesses.

This is our epitome of modeling. It was a very expensive program at McDonell-Douglas. We put in all the differential equations and we could pretty well predict what would happen if everything was the same. By that I mean that the material batch was the same. There is still some batch to batch variation that probably cannot be controlled. Then there were some extraordinary events. We ran

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the model and the autoclave and everything came out as predicted and then we made this nice thick laminate and everything went to hell and the model did not predict that. With the material that we modeled, we needed a really extensive database, properties as a function of temperature, thickness, material batch. Most models don't require high levels of quanitification. In my opinion the best use for models are to study what might happen if you do different things, to study the interactions between materials. But it is pretty expensive to do a model.

One of the ways that you can use a process model is with an expert system off-line. An expert system has an advantage over people in that it doesn't have any inborn prejudices about what to do with the model and it can run the model over and over again. With this program we did use such an expert system off line and did optimize it with the model and we came up with some real improvements over the current way we were making the thing. Depending upon the batch, we went from a 227 minute reduction in time to just a little over one-half hour. Those were real parts or sections thereof and they were in large autoclaves. I think this translates pretty well. This model ran over and over again and it had certain criteria that it had to meet. I don't remember the exact criteria.

One of the ways to find out what is going on inside is to use in-process measurements like the thermocouples and that won't cost you much. These are some of the things that we have been able to measure to this point. Temperatures and pressures. Dielectric monitoring has been around a long time. I don't like to call it monitoring. I like to call it measurement. There are some pretty

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sophisticated fiber optic techniques for pressures and stresses and we are now developing a technique that can detect the formation of void on fiber optic. The idea of patterns as opposed to measuring temperature or pressure is a very valuable one and probably the reason that we were able to do in-process control. We are now using an array of thermocouples which gives us a measurement of heat flow from the inside to the outside. We are actually doing it in the process. You know thermocouples are really small today and at McDonell-Douglas they use fiber optic temperature measurement. The dielectric sensor is really good for resin flow. One of the most interesting things that we found out was when it actually made sense to apply pressure. You need to look for a pattern in vitrification and gelation. If you look for a number, it will differ from batch to batch. Patterns are repeatable in materials from batch to batch and from material to material. We haven't done to much with thickness change in our organization.

The main point here is that you see qualitatively the inverse behavior in dielectric. Qualitatively is computable. Quantitatively, you are going to want to look for a number. There is always the process problem of identifying the patterns and interpreting them. Here I show granularity. If you take measurements over a certain amount of time, you get very different information from taking it over a little longer time. If you look at this segment of the curve and this segment, you would say that here the pressure was steady and here it is decreasing.

What can we use all this for? We can use it for model development and we can use it for in process control. You can also use it for

quality verification. We developed in house to use all these capabilities of process control and in-situ system-one that takes a sensor reading and automatically adjusts the process on the fly every thirty seconds or as required to get back on track towards our goal. That requires you to have goals and that you are able to measure at least some of the properties that relate to those goals.

Here process one is the cure cycle and process two driving home from work for me. If you follow those directions, do you think you make it my house? I doubt it. Our process strategy is something more like this. Here you have a road map, you have some road signs along the way-large temperature gradients, viscosity minimums, glass transition-places where you are going.

This is actually in production right now. This is the A-10 aircraft, my favorite aircraft in the Air Force. It is a good plane. They replaced these parts with composites and we chose to use this expert system to do the production cure. It was kind of a gutsy thing. We transitioned it and went from a 450 minute cure cycle to one that was a little under 100 minutes. Our properties improved and we estimated a savings to the Air Force of about $5 million per year. What we were able to do is make what we wanted. With the conventional method we were unable to make a part that didn't have delaminations. The panels we made with the conventional method, we could never make anything thicker than one-half inch without major delamination. With the expert system we made two-inch thick panels and didn't have any problems. With the conventional method they were not able get inside to see, but with the expert system at 26 decibels, we could see everything inside-the striations

around the circle are where we have transitions. It is a radial weave. You can clearly see everything that was in there and the materials were extremely good.

Like everything else, expert systems have their uses and they are not perfect. I think they are the best thing going to control batch processes because they can handle a lot of different variations and make judgements on the fly. I think they can be used by the designers and they handle exceptions extremely well. You have to have sensors and you have to know where you are going. You need to have some sort of expertise, but I think there is a lot of expertise out there in carbon-carbon.the thing that mathematicians have difficulty with is that it will work and work and work but you can't prove it.

Another in-process monitoring type technique that is really ideal for continuous processes is artificial neural nets. You have a bunch of measured variables coming and some target coming out. We use this on manufacturing of carbon phenolic film for prepreg. We did ours a little different than it is generally done. We made first the film, like you do for hot melt. This gave us much better control. This was actually done on production machinery. We did our experiments on a production machine and then we did our actual run there at ICI Fiberite-Greenville plant. We measured a lot of things. We actually ended up using fewer measurements than we made. The most frequent measurement was the beta gauge which is on most prepreggers already. This is what we got. Here I am cheating a little bit. Standard control is standard control for hot melt. I don't have figures for solvent, because you don't make a

film when you do solvent. If you look at the standard deviation, it was pretty exciting, I thought. Fiberite was not quite as excited because their equipment is not designed to work with an artificial neural net and it would cost something to modify that equipment and no one out there is asking for that kind of quality, so why should they do it. I will say this. I think that when it comes to control of processes, neural net is an excellent way to do the job. It does have limitations. You don't learn anything about the process and you do have to have a training set which means you have to do some experiments, about 27 runs.

This is a summary slide and I'm done. You can opt to do process control a number of ways. You can do it the way we do it now which is the A priori model which is trial and error. You have decided ahead of time what the proper cycle will look like and you run the process cycle every time the same way. You can also take a lot of statistics and feedback from that process and the third way, the way that we like, is to use some in-process measurements, making our adjustments in real time so that we build the quality in. The main problem with all of these techniques is cultural. Have you heard these arguments before? If not, you will. There are a lot of tools out there to improve processing and you need to make use of all of them.

Upton   Thank you, Frances. I am going to take just a few minutes to talk to you about something I know very little about. There is a new technique called magneto-optical mapper or MOM being developed by Army in Huntsville. These gentlemen, along with Dr. Tanton who is now with Teledyne Brown, have developed this along with

IBM to analyze semiconductor. During the course of development, they decided this would be a good thing to use technology utilization on and see where else this technique might be used. They came to our group because they knew we did test method development for solid rocket composites. They have some of our samples and we are waiting for them to be run and hopefully by the next meeting we will be able to assess a little better how helpful this technique might be.

Basically this technique provides spatial and analytical information obtained from paired and unpaired electrons. It uses IR and takes it quite a bit further and I know that IR has been very important to us in the past. There has been a lot of controversy about what IR has been able to tell us. IR is one of those tests that we are looking at as being a possible on-line test technique. They are using the Faraday effect and basically what happens is a plane of linearly polarized light passes through the sample which is in the same direction as the constant magnetic applied field and you see the plane of the light with a detector here which can detect and analyze the Faraday Rotation. Evidently this is the key. They found that this way they didn't have as much problem with their sample configuration. They got their answer quickly and once they had the setup, they were ready to go and they could run over and over. What they do is use a Fourier transform infrared spectrometer as a broad band light source. Here is a schematic of the experiment and here is the polarizer and the sample is here. This detector here they can change out depending on what the sample is. This is a very homemade looking instrument. We went over to the lab to check this out and they have a commercial FTIR and they just have it

patched together. We gave them film and they ran it and they had everything setup to be evaluated in the far IR region and they couldn't see anything. Now they have to reconfigure it to analyze in the near IR region and from literature searches that we have done, this might make sense, because there has been some work published where they have had some success looking at phenolic resin in the near IR regions. This could be promising. As soon as they complete a paper they are writing, they will change the configuration and reset this to the near regions and put in our sample and run it. Basically they ran this mercury, HgCdTe semiconductor and this is a regular transmission spectra. They information at about 1400 reciprocal centimeters. When they apply the Faraday Rotation, they were able to gain some more information in these regions. This slide is what really interested me. Basically what they did was run an uncured composite and they go this and then they applied the baseline corrections and they did get a spectra. Afterward they ran an experiment to see if they could detect a failed composite. the only thing about this example that I really don't understand is they compared a cured sample to an uncured resin. I am not really sure why they didn't compare cured to cured. What they are telling us from this is that they found that difference between the two spectra was in excess uncured resin. They concluded that for this material, by monitoring 1520 reciprocal centimeters, they in turn monitor the critical resin mechanism, so that they know that if they have too much uncured resin that composite will fail. This could be very important to us in cure monitoring and performance-based acceptance testing. I am very interested in running a similar experiment with our material. I hope by the next meeting we will have more information. This is

not costing us anything. They are out looking for people who will work with them so that they can understand the capabilities of this instrument that they have developed.

Day   I am going to talk a little bit about the current round robin work on permeability testing. We are in the middle of qualifying, at Corky Clinton's request, the ASTM D1434 unit that we have there at Marshall. I used to start this presentation with a quote from Corky that says this is a defacto standard aft exit cone that we have used to run the test.

Basically, Corky and I came up with this list of aft exit cones. All of these are Thiokol aft exit cones, tag end, machined by Southern Research. We added two other ones to extend the range of permeability that the test would handle. These range between the highly permeable ones are about Darcy minus 13 and the lowest was minus 17.5. That is quite a range/ We also added a graphite phenolic and a piece of 2219 aluminum. These were all selected because of the range and because they were available.

You can see here the range of permeabilities that we looked at, covering a range of 10 orders of magnitude. The chemical engineering turn-down ratio which governs what kind of a range that you can run on a process, well this is a huge turn-down ratio. It turns out that in the course of further testing we found out that approximately here at a Darcy minus 14.5 you go to what PMI calls the transition of flow permeability to diffusion permeability. The people involved in the test are thiokol, Southern Research and

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Porous Materials Incorporated. I had earlier reported on what they called a capillary flow porometer and that works down at the low flow range, but it doesn't work at the higher flow range. We had to go to a residual gas analyzer. A residual gas analyzer is a method of testing for flow that uses a gas here and the specimen goes here between stainless steel flanges, an inlet valve and then you have a gauge to measure the pressure on the high side and a gauge to measure the pressure on the low side of the specimen and also a gauge to measure vacuum on the vacuum pump. There is another valve to isolate the device. The reason that we used this particular setup is that you can, with the mass spectrometer, measure the target pressure of any particular species. This method lends itself to being able to perform higher dynamic temperature permeability specimens. If you put an oven, some kind of heat, here, you may or may not need a nitrogen trap to protect the mass spectrometer. Basically what occurs is you pressurize this side and then you measure the flow to the specimen here. The carbon phenolic specimens give of vols, water, alcohol, nitrogen, oxygen, who knows what all. In the standard technique for measuring permeability, basically what you do is collect all the gases and measure the flow rate. We can't differentiate between the off gas and the permeated gas. With this method they used argon and we were able to measure the partial pressure change through the specimen and from that you calculate the flow. The data that we generated looks like this. This is a real low permeability specimen and basically what we are seeing is the transmitted pressure in millimeters of mercury of the argon only. We got a high side pressure of 1014 Torr which after you open the valve, it dropped a little, but stayed constant after that. There is a rather long straight

section here. I went to PMI and we ran this actually in my presence and what we do is typically take the straight line section of this plot and calculate the permeability based on that. We thought there was an error because it was a really high number compared to the value that we had got at Marshall. Finally, the operator there said that if you take this slope down here which is different, maybe it will give you a different number. We ran that one and we got exactly the value that we got at Marshall. Basically what this says is that we can measure the permeability based on just measuring the permeated gas without the off gases. The permeability is a little more complex than we have seen in the past. Apparently it depends on how you measure it which is what you would expect.

There is a definite change in slope here and by the way, these data are taken every 10 seconds.

Pinoli   The way this test operates, when do you start the time?

Day   When you open the valve and it is all computer controlled and operated.

                The pressure on this side starts at 1014 Torr and when you open this valve, it drops a little bit.

Pinoli   So essentially you are pulling the vacuum upstream.

Day   Well, yes.

The round robin was split into two parts for contractual purposes. The two parts were under $1000 each and we were able to do it on a purchase order. That way, we were able to generate the data quickly. I think I am paying the price for that in results. We had really good agreement between ourselves and Southern Research, but not between ourselves and PMI. I think the reason has to do partly with the method and I was there and I think they were trying to hard. These are the results that I got. The purpose of doing this is to get the data quickly and the price we paid for that was that we could not afford to run duplicates. These are all single point numbers and they don't agree well with what we got from Southern Research and from Marshall.

Pinoli   They are all based on long term, right?

Day   Yes. These are calculated on the initial slope. We did that every time because we had to have a consistent way of calculating permeability. If we went to a different slope, we would have gotten different numbers.

Pinoli   Somebody could argue that these are transient conditions down here and these are the only standard conditions.

Day   That is true and let me give you the rationale why we selected that in the beginning. The point in measuring permeability is because it is felt by shuttle engineering that permeability is a strong player in the ply lift phenomenon. The lifetime of an ablater in a rocket nozzle is under two minutes. I picked down in the that bottom region for under 5 minutes because I figured that was more like the

real numbers. It probably was not the best for generating real stable data. It's not what PMI would have done. When they did it, they naturally picked that longest slope and told me that they do that routinely. That initial slope is observed in every permeable material. They think that it has to do with the crud that is in the pores and it takes some time for the permeating gas to get through that.

Abrams   Were the MSFC and the SRI techniques the same?

Day   We are using what is called a volume increasing method and I believe that Eric is using a pressure method, but they are similar in that they are, as PMI calls them, accumulating methods. Where as the PMI method is an instantaneous method. A problem that PMI was having was they took the specimen and they took out the holder from the capillary flow porometer and they were having a little trouble with having it flex. You can't have the specimen move. The remainder of the runs will be done when we get the funding.

In the previous quarter, we worked with the RSRM office and we had begun testing and we realized from work that we had done with Eric that our results weren't very good. Some of the specimens that we were measuring were taking up to a week to get results and you could not tell when you did them twice that the numbers would be this bad. We weren't getting good agreement at all. The first thing that we did was modify our specimen holder so that we could get a standard size. We also went out an found a series of sizes of flow lines because we felt we could get better precision on small flow lines. We got some larger ones, too, so that when we measured this

material we would get 17 cm of flow in under half a second and be able to measure it. We modified the procedure. Formerly you were limited to 1 atmosphere of pressure differential, now I am limited to 30. We have a precision pressure gauge in the system but we have to work through it. The most controversial thing that we have done is eliminate the water bath.

This is straight out of the ASTM with a couple of different things. We have a gas source that is using primarily nitrogen or helium. The test fixture is stainless steel with an 8-inch diameter that fits into a water bath to maintain constant temperature. The permeated gas enters the bottom of the test fixture and we have an aluminum plate here to hold the specimen and there is an o-ring below that to make sure that we get good seal. The gas then flows up into a capillary tube and then what you do is measure from the time you turn the valve on how long it takes for the indicator in the capillary tube to go a certain distance. One of the things that we found was that room temperature was about 22° but the water bath was between 25 and 28, 29°C. We fo. . that we were getting a thermal gradient in the water bath above the capillary tube. We didn't really put much importance to it until we looked at the data. I will show that to you in a minute. The pressure on this machine can go no higher than 180 psi because of the plumbing that goes to it, but we set it no more than 30 psi because we have a precision gauge.

Abrams   What do y   ink the pore pressure of some of the materials is?

Day   I can't even begin to answer that question.

Hill	Do you mean pore pressure during his testing?
Abrams	When you are firing nozzle, what kind of pressures are you trying to measure permeability in?
Hill	5000 psi is a ballpark figure.
Abrams	I think that is important when you start figuring stuff like this. If you are looking at permeability at very low pressure, it can be quite a bit different.
Day	Yes.
Hill	If you don't have permeability at low pressures, you will surely have higher pressures develop.
Day	ASTM D1434 has a little rider on the side that says this is semi-quantitative at best. The second thing that they discuss is that the reason that they pick 1 atm pressure across the specimen is because they were very concerned about changing gas properties across their test. I will show you that later. We are very dependent on the viscosity of the gas, the density of the gas. If you have really high pressure differentials across the specimen, then the gas properties will change. That is a major concern. I can't evaluate that right now. I can only go 30 psi.
Abrams	If you are looking at something that will give you a feeling for how the part might perform, that could be a significant factor that is not being taken into account.

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Day   I think you are right. What we need to do is get the capability of getting there. I can only go to 30. I would have to take a specimen and measure under very low pressure differential and then go to a higher pressure differential. I have not done that test.

Hill   Part of the answer might be when you do the elevated test, elevated temperature.

Day   Yes, that is true. Pressure, temperature and volume of the gas are all related.

Abrams   The other issue that I would mention is that although argon is really good with model compounds, it is highly unlikely that argon is a constituent in you problem.

Day   The only reason we picked that is that we know it is not off-gassing. I don't think there is any argon, that we have significant quantities of argon built into our carbon phenolic.

Pinoli   Frances, you are a good lead-in to the Karl Fischer work.

Day   Anyway, this data right here is the basis for dumping the water bath. We ran a series of tests with the water bath and got some pretty good results for the first hour and then we took a lunch break and came back and all of a sudden our numbers started doing this. They started climbing on us. We had been ascribing that to leakage. We thought we were getting water in there, so we shut it down and took it apart. There was no water. Then we thought we were either bending the specimen or the o-ring was being

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compressed, or something. We were having some sort of change in there. At that point is when Bill, the technician, said that it was a lot warmer there and that is when we measured the temperature across the capillary tube. It is a full degree different. One degree difference in that water bath is enough to change the direction of the flow and it will literally go negative. At that point we decided to try it without the water bath.

The next day we tried it without the water bath and we found something really extraordinary and that was that the standard deviations all of a sudden got really good and, not only that, but they held for a long time. We did have a problem in that we had to make sure that our analysis times were not short. We will never be able to do another of these long runs because I have to have the room temperature constant. I have to have isothermal conditions. If the air conditioner comes on in the middle of it, it will wreak havoc. By the way, the permeability of these on serial number 78 do not match the actual numbers that we got for the specimen when we ran the test finally, because I was using the wrong cross-sectional area.

| Thomas | Tony, second from the bottom, you have a 1.007. Is that an outlier in flow rate? |

| Day | No. There was a slight pressure differential and what you get is same time lower flow rate. |

| Bhe | Is the PMI data and your data from the same specimen? |

Day   They ran the exact same specimen. They were all identical specimens. Handling was a problem. Here is another experiment that we are running right now. How many times can you run gas into a specimen and not dry out the specimen?

Hill   What gases did you and Eric use?

Day   We were using nitrogen. I don't know what he used.

Stokes   Argon.

Hill   Do you typically use argon?

Stokes   No, we can use argon or nitrogen. It doesn't matter. It is independent of the gas that you use.

Abrams   This is another case when the model and reality aren't very close.

Stokes   We are looking at properties on the as-cured material. We are not looking, at this point, at properties of the material at temperature.

Abrams   I recognize that. That is why I say it is not very close to the model, or the model isn't close to reality. Real temperatures are several hundred degrees higher.

Stokes   Right.

Day   This is a test. What I am trying to do is answer the concerns of shuttle engineering.

Abrams	Do you think this is the proper way to do that?
Day	Personally, no. We have lots of data to support that. However, let's talk cultural. There are people at NASA who have great faith in this particular test and the results as a predictor of performance. All I am trying to do is to bring up the testing at another place to accomplish their desire.
Stokes	You have to be able to do the room temperature test first.
Day	I understand all of the objections to this test, but....
Abrams	But does somebody else understand that? You are saying to me that this is the not the test you want to end up with. This is just something to get you there. Is this being accepted as the test?
Day	What I am showing you is the hoops that have to be gone through in order to call something qualified. We need to be able to do this at heating rates similar to what a nozzle is seeing and loading rates similar to what a nozzle is seeing. Right now, I don't have that test. The community doesn't have that test.
Upton	One thing that I think needs to be pointed out is that you have done this work. Some of those people that have been vocal about this being the performance predictor have quieted down. I think you are on the right track. You are on the right track because you are trying to show that this is not *the* test. This has really been crammed down Tony's throat.

Day	I am not convinced that the room temperature is really a predictor of what happens to a fired nozzle.
Mills	There are people who have made decisions, or who are making decisions, that a number of -17 at room temperature should not be flown. It should be put aside until we further understand that.
Day	You have just stated the current situation.
Abrams	Given the lack of other data, that may be an intelligent decision. It may not be. We don't have enough information, but I...
Pinoli	Unfortunately, before we go any further on that, we have performance on hardware that is just the opposite. It suggests that -13 is the one that is going to get you into trouble.
Day	Put it this way. We have testfired this nozzle with the -17.5. That has been testfired. We cut the aft exit cone and it looks fine. There is no plylifting.
Stokes	One of the problems that everyone is doing is assigning that permeability number to the entire nozzle. That cannot be done.
Day	Permeability is a dynamic thing. We have yet to take a full nozzle and cut it up and run 400-500 tests on it. That is being very seriously considered.
Stokes	We already have data on a very small tag end that ranges over two orders of magnitude. You can imagine what it is in an exit cone.

| Day | Here are the preliminary results. This is some data that I generated last week that wasn't in an earlier presentation. We compared pretty good to Southern Research. The PMI numbers are not that good. The interesting thing here is that we got a value for 2219 aluminum, which is the reference material, and we actually got the high value on that, -21.08.

Here is the latest printout. You can see the comparisons. I don't have an explanation for these differences here in the PMI numbers. We probably ought to run, which we are going to do, in triplicate this time. This one here looks like fantastic agreement. In fact, when you see the rest of the data, it is really a lousy value. Here is the high, low and average that we measured. We have difficulty on our unit measuring very low permeability and very high permeability. We were at the edge. We ran some of these many times. |

| Bhe | On the same sample? |

| Day | On the same sample. You can see that we got reasonable repeatability except on this one and basically what happened there is like before lunch and after lunch. I think we have a high end problem and a low end problem on this test method.

There are some final things that still need to be done on this test. The capillary tubes, I just sort of had to buy the ones that are available and I have just this week received some that actually fit. They had to be specially made. We need a new pressure gauge that will allow higher pressure so we can examine the pressure problem. |

We need some kind of temperature control. I need to finish developing the Forcheimer equation so that we can actually tell whether the data that we are generating is any good or not.

The way that we calculate permeability is by this equation. Our first assumption is that we are isothermal ideal gas and our second assumption is that if we can just get viscous flow without inertial effect, then all of this goes away. This is what we are calculating right here. You have to have constant viscosity, constant temperature, constant density, ideally a constant flow rate and a known thickness, and we have to have the known pressure. If these are not okay, then these other elements of the equation kick in and I have not developed that yet.

We have seen some really strange things at low permeability. One of them is pulsations. The capillary will be going along real nice at some low flow rate and all of a sudden stop and stay there for some time period and all of a sudden it will take off. A bubble forms on the surface of the material and then bursts. PMI runs what they call a bubble point test. I don't know how dry the carbon phenolic is and the amount of water, stuff in carbon phenolic is a subject of debate. What I am assuming is that the stuff that is in there bubbles on the surface. I don't know that, I am just assuming.

Specimen handling has its effects. PMI got this number and then left the specimen over the weekend and got that result. Eric gave me this information. They said that serial number 7 was polished

on one surface so that they do an examination of it and you might want to compare those numbers.

Thomas   Do you have permeability numbers for 7 and 113 before they were polished?

Day   These are the numbers here.

Thomas   It seems to me you are saying that it is the surface.

Day   Surface is involved. This is a legitimate change, but I don't think that is. The thing that we should remember is that it is a test and not the actual material. Does anybody have any questions?

Pinoli   Frank, you're up.

Stone   These are the sample numbers. F means forward and A means aft. These are the samples at either extreme. Marshall ran fourteen samples and they got 103 measurements on those 14 samples. That includes the aluminum and carbon phenolic. SRI did 12 and they have 12 and PMI did 9 and had 12 measurements on those 9 parts. These are the averages for the samples that everybody ran. This standard deviation is of the averages of the samples. SRI is very close to Marshall, pretty good agreement. PMI's data does not have very good agreement.

If we plot the Marshall data against SRI data, this is what we get. The correlation coefficient of 0.983 and this is the least squares equation. One thing that I want to point out is the slope. They are

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tracking each other very well. The intercept, which is this number, represents the offset, or bias between the two measurement systems.

Day   That slope agreement could be because it was not a blind test.

Stone   Yes, if that kind of entered into it, if your values were influenced because you knew Eric's.

Day   It might have been.

Stone   This is PMI data against MSFC. The correlation is 0.524 correlation and a very wild regression equation. It looks like #7 birdshot. This is PMI versus SRI values and since MSFC and SRI is so close, you get virtually the same thing.

One of the things that you can ask about these things are how good are these measurements? What is the measurement uncertainty? I had 206 data points from MSFC and I got this number and Eric supplied me with 9 measurements, run be different operators, on different machines, at different times and I got this, which is about a third of the MSFC number and based on only 9 points. I'll show you what that looks like. This is a technique called intraclass correlation. What we do is compare measurements by plotting one time as a x,y and another time as a y,x so it is reflected by a 45 degree line. Variation along the 45 degree line is variation in parts and measurements. This is a visualization of the numbers that Tony gave earlier. This is the carbon phenolic and this is the 2219. What you can see is that SRI and Tony are very close.

Upton   But not PMI?

Stone   Not PMI. Any questions?

Pinoli   Frances, I am glad you are still here. I think some of the questions
                   you asked earlier fall into the area of the Karl Fischer and what we
                   are trying to generate with Karl Fischer analysis.

                   The objective of the Karl Fischer work is to assess the potential of
                   Karl Fischer to provide performance related data. The type of data
                   that you can get out of Karl Fischer-total residual vols measured at
                   isothermal temperatures 325, which is the classical temperature
                   which we measure residual vols or 500°F which is pretty close to
                   the upper limit of the apparatus' capability. We can also look at
                   total moisture effusion at 325 and 500. We measure the ratio of
                   moisture to total volume and we can give you a moisture effusion
                   differential rate versus time plot and a cumulative moisture effusion
                   versus time plot and initial moisture effusion acceleration rate. I
                   don't know how accurate that is at the present time. In most cases
                   the rate at which the moisture comes up is quite high and you have
                   to look at that area very carefully.

                   Before I get into the apparatus, I wanted to throw this up which
                   defines the sample size that you use for Karl Fischer. We typically
                   like to make our cuts in-plane. It is 7mm x 7mm x 7mm which is
                   roughly ¼"x ¼" x¼" and we have the three directions, warp fill
                   direction, either BB, AA and off-ply direction, C. We know from
                   a lot of moisture adsorption behavior studies that the moisture

intrusion and the effusion rates are about 10x different going through across-ply direction versus in-plane.

The test apparatus that we used is a standard commercial item. This flow diagram is not the world's best for simplicity's sake. We inlet nitrogen gas through a double bladder system which pulls out any residual moisture that might be in the gas. It carries into a glass container, quartz, that flows into a heated oven chamber. This is a resistance-heated, glass-walled vessel which is heated by putting resistance on both ends of the glass. This is high conductivity glass that reacts just like your resistance element in a conventional furnace. Not only do we heat the oven very uniformly, but we can also look at our sample which is brought in through a quartz probe located out in the cold zone through a little port. We pull the plug out and drop the sample into the boat at room temperature and once we press the automatic position, the boat moves directly into the isothermal oven. Automatically the gas passes over the sample into a retriever tube and back into the titration cell and the device automatically measures the quantitative amounts of moisture that are being evolved from the sample. We can set the oven temperature at 325 or 500. We have run them both on numerous occasions. We have a lot of data. We generally prefer to run the test at 500 because I think it is more meaningful. We develop a lot more pore pressure to get the moisture out of the sample. I think the pore pressure phenomenon that we are able to duplicate gives you reason to believe that it is closer to the real world that we are trying to study as opposed to a room temperature specimen. The Karl Fischer apparatus is actually measuring the effusion of water as it

is being forced out of the sample. I think it is closer to real world.

This is the test procedure. We preweigh the sample to a roughly 0.1mg. We directly introduce it to the room temperature quartz boat. We do not place it into a boat that has not been allowed to come back down to room temperature. We press the start button on the device. The data acquisition system in the device allows us to pick up 120 data points, so if you program it for 2 hours of operation, you will develop rate data on the basis of 1 minute intervals. If you want to concentrate the data to 30 minutes of moisture effusion, you can set it at 15 second intervals. Obviously, it depends on which way you want to go and which way will give you the data which is most interesting to study. We have tried to run this test in such a way that it can be used as an acceptance test sometime downstream. The purpose of Karl Fischer was to understand the nature of the material as best we can, but also be prepared to ultimately say that we can transfer this over to an acceptance test, trying to keep it as simple as possible to keep operator error out of the operation. The data that we get out of the apparatus is moisture effusion rate versus time. I will show you some plots on that. After the conclusion of the test, it is automatically extracted from the hot zone and allowed to cool at room temperature. After it has reached room temperature, we weigh it. From the initial weight and the final weight, you get the total mass loss which is total residual vol loss for the sample. We can then calculate the weight percent of total moisture effusion, weight loss and then we calculate the percentage of moisture that

came out. The apparatus automatically gives you the milligrams of moisture that are liberated from the sample.

In the past the type of the data that we have presented is 2 hour data, 500° F isothermal, total water involved, total volatiles involved and water involved in the total vol number. In a case like Cowl 17, we had 3.58, 4% total vol, 89% of the total vol was water. What we did on a sample like HDHU, the baseline panel to be used for experimental work at SRI, we found that after two hours at temperature, there was moisture being evolved. We placed it back in the device and picked up another 10% water coming out for the second two hours. This is old Avtex. Generally what this gave us is a good feel that the moisture levels were not varying a lot with regard to any sample that we were dealing with.

Moving on to the rate data, this is data that was developed at one minute intervals. These data points that are indicated are values that were used for identifying the curve. There are actually 10 data points located between 1 and 10. Keep in mind that what you are doing is rapidly coming up to temperature. It reaches a saturation point. The device can only measure a certain amount of moisture and any that is left over once it has maxed out is picked up on the sequential measurement. When the dropoff occurs you begin to get real numbers. One can extrapolate on this curve and get a pretty good feel for the rate change that occurs. This happens to be for background. This is a sample that was taken out of a 504 ring, identified as 6071 by SORI. It was cut out between 315 and 0 degrees. Another sample that I am using for comparative purposes

is the 23 HRPU, which refers to the precursor background in that material. Eric can probably tell us what it is.

Stokes   Hitco, rapier loom, Polycarbon.

Pinoli   Here is a material, same temperature, 500°F, isothermal, same sample size. You can see that it reached a maximum here of 2.3 mg per minute release of moisture. It topped off very quickly, but still after 120 minutes a quantity still coming off the sample. Finally a third sample which was an Avtex aft exit cone 17A to show that if you overlay these three together, this is a range of the data. There is a tremendous range in the ability of the material to release the moisture during isothermal exposure to 500°F. Another way to look at the same data is cumulatively. Since we didn't know which way to go, we felt that if we just built the computer code up in both avenues, but we are still vacillating back and forth trying to decide which one we prefer to use. Here is the same situation where the 315 ring had a very fast evolution. Now we have something else to look at. We can look at this coming up here. We can use a thirty minute discriminator. This is just chopping off the data at thirty minutes and if we are interested in the effusion of moisture in the initial phase, we can get a lot more data in this region if we think that is important. One can try to establish slopes for each one of these lines. We can use ratios between here and out here, or we can consider another factor that comes up in the next curve. This temperature rise refers to the rise of temperature on a thermocouple that is imbedded in the sample in the center. What we wanted to do was to know the time lag between the surface of the sample and the center of the sample. If we are going up to

325°, you can see we are approaching 300 at something like 420 seconds. At 500°, I think we are getting very close to 6 minutes. At 6 minutes the entire sample is isothermally conditioned. We are at steady state. If it takes 6 minutes to reach isothermal conditions, we can go back to this cumulative curve and simply say that we can ignore all of this data up to about 6 minutes. We can throw it out and essentially look at the curve that develops after the 6 minutes when you reach isothermal conditions. This is the portion that we want to look at. From that you can do some calculations on permeability, the ability of the moisture to get out of the sample due to pore pressure. Part of the initial program definition was to set some ground rules. We will have to set some limits, prejudgments on limiting the test procedures and try to set some criteria. Some of the ground rules are as follows. We are not interested in just testing material for material's sake. We need very well characterized material to work with. We would love to have permeability data on it. We would like to have mechanicals, fiber precursor, prepreg, etc. We want to know as much about the history of the sample that we are testing as possible. We also would like to say if it ply-lifted or it did not ply-lift. We do have a lot of tag end material that we can look at with that respect. All testing will be performed at 500°F. The Karl Fischer test is pretty clear on the issue of temperature. 325°F simply does not build up enough pore pressure in most samples to get the majority of the water out of the sample. It would be misleading to say that this is the total water content of the sample if you look at a short-term 325 test. Rather than waste a lot of time going at low temperature, we are going up to 500°F. There seems to be a consensus in the industry

that pyrolysis does not begin until you exceed 500° F. The polymer isn't breaking down until you exceed that temperature.

Brown   Pat, I know you have some data at 325. What kind of number will you see at 325 as compared to the 500?

Pinoli   Generally about ½% difference higher at 500. Tomorrow I will talk about some prepreg data that I generated on the low density prepreg. That was interesting because looking at prepreg with the low density program, I saw the same moisture content at 325 as the 500. Every time that I have looked at a cured standard material, I typically see about ½% difference. The question then comes up, why are we seeing a lower amount. Is it because the moisture cannot diffuse out or is it that the higher temperature condensation reaction? It has always been a theory that there is some unreacted constituent still in the material. The low density prepreg suggests that is not the case. The only reason that you are underestimating the moisture effusion is the fact that it hasn't built up enough pore pressure to get out.

               Wasn't there a secondary exotherm that we were looking at? The DSC was showing a second exotherm.

Day   The primary one was about 30 kilocalories and the secondary one was about 6.

Pinoli   Was it well-defined?

Day   It is definitely there.

Pinoli   Somewhere around 350?

Day   The second exotherm occurs, barely occurring at around 285 or
                290. I don't have the scan in front of me. Maybe 300.

Pinoli   Back to our ground rules, we are going to get moisture effusion rate
                based on 1 minute intervals. We are going to get differential rate
                data and we are also going to get cumulative. I might add here that
                right now we are looking at a method for calculating the
                permeability after you have achieved isothermal specimen
                conditions.

                The recommended approach will be with tag end material with
                heavy emphasis on ply-lifted tag end material and normal ply-lifted
                material, preferably large rocket motor firing, maybe M-NASA
                motor firing if necessary. I am also going to go after virgin
                material. That is more of a wish list, but if it is possible to extract
                a virgin piece of fired material, that would give us a very positive
                tool to verify the observations that we think are happening. It is
                much easier for us to find fired hardware out there to analyze and
                verify. On the RSRM motor, the forward end of the aft exit cone
                is overdesigned even I can't believe it. It must have about 2 inches
                of virgin material still left. I also want to go back and look at the
                ASRM Karl Fischer data base on the standard density material to
                make sure that I have gleaned everything that I can out of that.
                Then I want to move on the these samples that Tony has finished
                looking at that have been used for measuring round robin
                permeability. I will also run Karl Fischer analysis on the same
                samples and look at the effusion rates of moisture. I will also look

for relationships to see what lines up and what doesn't line up. One of the basic questions to be answered is whether moisture effusion characteristics from data generated are comparable to the permeability numbers that are being generated. There is a lot of feeling out there that we are looking at two different phenomena with each test.

Thomas   Pat, are your earlier charts saying that you were able to get only about 3.88 % moisture out of there and whatever else is left in there will be driven out by the pore pressure?

Pinoli   It's pore pressure that is driving the moisture and the vols out.

Thomas   What is the total content, moisture content?

Pinoli   In the nozzle? The data that I have given you is a pretty good indication of what you are going to see in hardware.

Abrams   Pat, I have a couple of questions. How long does the firing take?

Pinoli   120 seconds.

Abrams   Two minutes. That is two data points. What is the change in temperature during that time?

Pinoli   The heating rates, I'll let Eric talk about heating rates. What does that break down to?

okes   The heating rates of the nozzle? I have heard everything from 50°F per second to 200°F per second.

Abrams   The point that I would like to make is that I think the most interesting part of your whole thing would be the initial heat up rate, not the isothermal part. Perhaps there is a limitation to your equipment in taking data every one minute, but things are changing every second. The temperature is going higher faster than what you are measurin.. It is .ne old difference between equilibrium processes and non-equilibrium processes. They can have very different behaviors that may not bear any resemblance to each other. You show that to a certain extent with your curves where you see the really sharp rises on some materials and on the other materials the rise isn't so sharp.

Pinoli   The reason I began to get this illusion of the initial part of the curve was the fact that the theory holds that that is the good part. You like that part. Moisture can get out very quickly.   The part that you don't like would be one like this. It can't get out. In that case I could pickup very good definition in this area.

Abrams   Those are a totally different ends.

Pinoli   That is right.

Abrams   They are not the same thing. They are not performing the same, they are not seeing the same temperature rise.

Pinoli   The temperature rise, these samples were put into the same oven.

Abrams	I mean if you are talking about their purpose and why. This is one of my concerns. A lot of these tests that you are looking at as predictors of performance, you are looking at in totally different regimes. It is like saying you are going to measure laminar flow somewhere and predict how a propeller is going to perform in turbulent flow. They are not the same thing at all.
Pinoli	I can't deny your argument on dynamics. It is such a dynamic event and that we will never be able to interpret the data from it.
Abrams	That is not what I am saying. What I am saying is that it is a very dynamic event and that it probably important to look to some way of measuring that. It might be kind of scary to hang your hat on another regime all together. I don't think it is impossible.
Pinoli	I think every approach at the present time to identify a predictor of performance is counting on some analog relationship, whether you call that a permeability test at room temperature or high temperature, a Karl Fischer test, a residual test. Most of them are analog. They are looking at something that will give you a feel for it.
Mills	On the analog, are you going to apply single tests to all pieces of carbon phenolic, whether it is an aft part or a forward part? The 0.1 of an inch of an entrance cap that is exposed to the fire will see 4000°, 0.1 inch penetration in 10 seconds. An exit cone is different. It might survive with a different set of residual vols. Will a single test apply to everything?

Pinoli   What is the problem that we are trying to address with the performance? It has to do with ply-lift. It is the only issue that I see on the table. 99% of the time, ply lift occurs in aft exit cones.

Hill   In the SPIP 3 M-NASA test, we had ply lift in the housing insulator.

Pinoli   There is that isolated case of where it has shown up somewhere else. AS far as the RSRM motor is concerned, the dominant issue is ply lift in the aft exit cone. The heating rate in the aft exit cone is probably the most benign of anything that we are dealing with.

Abrams   That is more of an answer to my question. You are looking for a benign heating rate. Why don't you look at that rate?

Pinoli   Mainly because the apparatus that I have can't do that. Unless I get a million dollars to give to SORI to build a device, I can't do that.

Day   It is not easy to do that. You probably have just hit the quintessential problem of any of the nozzle testing.

Abrams   I agree that it is not easy to do that, although I don't think that it is totally impossible because you are heating your sample at some rate. You can't go 0 to 50 without going through a region. You are showing that and then discarding that region and only looking at the isothermal region.

Pinoli   In one way I am discarding it and the other way, you will note that there is a very strong relationship to the decay rate that shows up

after 6 minutes. I am not totally ignoring it. What I am saying is that I can get the same relationship by looking at the decay rate and then I am out of here. This is much easier to define and it is a steady state condition. You can defend this data from 6 minutes on a lot easier than you can defend the initial data.

Let me finish up so that we can go on. On the product of effort, number one was develop performance related tag end acceptance test for ply lift. Ultimately if that works out we want to work back to the prepreg to see if we can fingerprint the prepreg by using the same test technique and finally go all the way back to processing.

Upton   One of the things that I didn't mention this morning is the current chief of RSRM is being moved. We are about to get a new chief engineer. This may bring some new and different philosophies to the program. By the next meeting it may throw a different light on a lot of the problems that we have now. The new guy may want things implemented earlier.

Pinoli   We had a meeting scheduled in April to redefine the program. We have identified the samples to be tested. I am waiting for samples to arrive in the laboratory. We have about two months to do the testing and finish up the program by August. I am sure that we will meet the schedule.

Stone   Any discussion of number crunching gets back to that nasty word statistics. Any time you talk about statistics, you talk about the normal curve. You have to ask yourself sometime, what is normal about it. Why is it normal? It turns out, as Frances said, it is a

model. It fits a lot of things. This is an example of things it doesn't fit.

Any time you talk about the normal curve, you talk about standard deviation. What is standard about the standard deviation? The best definition that I can give you is the inflection point on the bell curve. When we normally assess things as to whether or not they meet a standard normal curve, we generate a histogram. What I have here is 5 coin tosses. At this point we have no heads. We have one head in 15 groups of 5 tosses. We have 2 heads in 32 groups of 5 tosses. Three heads, four heads and here all five turn out heads. The coin toss does not fit the normal curve, but this is one of nature's great gifts. Averages drawn from populations that are not normally distributed, we can average the normally distributed.

Here is what a normal curve looks like. These things are a real bother to calculate the area under. You have to use a Taylor series and all kinds of stuff. That is a driving force for using a normal curve. Someone has gone to the trouble of finding out what the areas are at various points in the curve. We don't have to.

Statistical notation, we talk about samples and populations. Samples are what we have been dealing with here. All the data we have seen today has been sample data. Population data is more hypothetical. We don't know what it is. We always estimate it from the sample. They use different symbols for it. They usually use Greek symbols for the populations and they are called grounders. We use Roman letters for the samples and they are

called statistics.

Some of these things are biased and some aren't. The variance, which is the square of the standard deviation, is considered unbiased. Let me show you why. Suppose I had two groups, one with a variance of 25 and the other has a variance of 49. One is about double the other. When I take their square roots to find the standard deviations, I get 5 and 7, quite different ratios. Statisticians will tell you that variance is a better measure of dispersion than the standard deviation.

Sometimes data is not normal, but we can make it normal. In the case of residual volatiles, Thiokol said the residual volatile data lognormal. That means that after a log transformation, taking a log base 10, it comes out looking pretty normal.

Measurement is a process just manufacturing something is a process. In the case of a measurement, what we are manufacturing is a number. That is the product. It is fair to ask how good is that product. What is it going to do for me? All the things that we apply to manufacturing distributions and that sort of thing, we can apply to measurements. You just have to know what the expectations are.

CPK is a measurement. All this CP does for you is tell you the relationship between your spec window and your process window. CPK tells you whether or not your process is centered in that window. If I have a CP of 1, that doesn't tell you that I am making

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goou parts because I might have a mean way out. CPK is a good measurement.

Errors, random or chance, affect things like precision, repeatability, and reproducibility. Then there are systematic errors and that affects things like the accuracy of bias or offset.

One of the problems in dealing with errors is that you only have available to you an observation. That observation is composed of the true value plus some random error. You might know what both those things are, but you might not. The expectation is that the average of a bunch of these observations will give the true value. If it happens that all the errors come out to zero, it may or may not be true. There are ways to test for that. One of the things that we can do to test a measurement system is look for that intraclass correlation which is what I did with Tony's data. I'd like to explain to you now how I did that.

If I have a couple of readings, 86 and 103 and if I plot them as x,y and y,x, I begin to get a collection of points and these points reflect about a 45 degree line. Those are both measurements on the same part. The units on the x and y axis are identical. When you do this with a bunch of points that basically fit the elliptical zone here and you can do a regression and a correlation on this thing. If they exactly track one another, the correlation is one. If they don't track each other at all, the correlation is zero. If one goes up and the other goes down, the correlation is -1. It is basically a cosine function. What we would really like to know, is the ratio of the minor and major diameters of the ellipse. Using the correlation

coefficient, r, you can figure that out with the discrimination ratio. If a correlation coefficient is 0.8, the discrimination ratio is 3. In that case you can divide your parts into the high, medium, and low. Tony had some that were about 18.2

Day   So we could divided that into 18 different....

Stone   Yes. That is not bad.

Hill   Is that his data versus SORI data?

Day   All I am doing is comparing Tony's retest. That is all this intraclass correlation coefficient does. For Eric's data, I had 9 values. All I could do with that was find the average and the standard deviation.

Here a bunch of different correlations of two variables, one plotted on the y axis and one plotted on the x axis. They both have a mean of zero and a standard deviation of one. As the correlation increases, you can become more and more elliptical. No correlation, and you get a circle. Sometimes a useful thing to do is take a correlation coefficient and square it. That is called the coefficient of determination. That tells you how much knowledge of one tells you about the other. When you get up to, say, 0.99, knowledge of x tells you 98% of everything you need to know about y. You can use one to predict the other.

At this point I would like to have my partner, David Kinchen, tell you about how you should do a round robin.

Kinchen	I want to talk about ASTM 691, interlab study, how to determine your accuracy and those kinds of things. There are statistics packages out there that will do a fairly good job. There are several good books out there evaluating measurement processes.

What most people are struggling with is measurement. Before you go off and do some process improvement, you should assure yourself that your measurement is telling you what you want. One of the things that has to be done in order to do that is to decide what is a meaningful level of discrimination. You probably need more than a go/no go level of measurement. I don't think that would be adequate for what this group is trying to address. There may be no single measurement that will tell you what you need. One of the key things that a measurement wants to do is provide you a meaningful level of discrimination. Two issues we have heard about today is do the raw materials conform to requirements, more importantly, will the end product perform. I think many of the tests that are done and the data that Frank and I will look at need to be looked at regarding this performance requirement. I asked Frank if there was a centralized data base as yet for all this information. You have an awful lot of measurements and there is no centralized data base.

In your measurement system, you would like to be able to separate parts or lots. There are differences that come about in the measurement process that you would really like not to have. We need to try to minimize these effects so that you can maximize the value that you have.

Basically the definition of measurement is the act or process of measuring or some figure or amount obtained from that measuring. In order to get a measurement you need basic things, a procedure. I heard you talk about that today. You are going to do some video tapes, have a written procedure. It is very important to have clear procedure. It must be understood. It must be all these things right here. If that procedure can be applied at different labs and by different operators, it must contain all of these items: written, clear, concise, unambiguous, descriptive and prescriptive, detail steps and sequence and so forth.

Pinoli   When we work up these video tapes, they tell us it can't be any longer than 12 minutes or people will go to sleep.

Upton   They actually just want 10 minutes. In the test methods manual, we can put what we want in there. We can go into detail as much as we would like.

Kinchen   I have heard a lot today about materials handling, conditioning of samples. I have heard about calibration, setup. Calculations and reporting format have been mentioned today.

Stone   They have touched on units of measure today, too. If you are measuring things that are two feet long and your only measure is a yardstick, you can't tell any difference.

Kinchen   Familiarity with procedure, that can be letting someone practice on it a couple of times.

When you start getting into consistency, that is relative. What you are looking at is some measurement that you have repeated over a period of time. Most of the studies that you do, the consistency aspect is evaluated in a lab and you are looking for repeatability. If you do the analysis repeatedly, you want to be careful that if you one your test on one instrument and one time you go to another, you recognize you may have some differences.

I have heard this touched on today, bias, relative characteristic, comparing results to a known value. Frank said he could compare MSFC to SORI's data.

One thing I wanted to touch on and I guess I will have to punch it real briefly here is to identify those things that you want in your study. Typically you have some parts you want to replicate. Here you have some trials. Operators can be anything, literally two different people running the same instrument, two different labs, two different methods. Another thing that is important is to randomize the order of these parts.

This is a little exercise that we went through. My background is not chemistry or chemical engineering, but with metals and materials testing. In this process the gas flow to the welding torches was critical to the weld process and stability. They had a technique that they had been using for over 10 years. They were evaluating problems and what might be impacting the welding process. They decided to put some teams together and look at the process. They went out and measured some parts, 3 different operators and 3 different tools. These are the results and what you

see is that tools y and z are very comparable, reproducible. What they found was, to their surprise, that some of their tools don't produce very reproducible parts. Tool x stood out unbelievably. If you look at this by operator or by part, you don't see any of this separation because it is not being looked at from the right view. Another way to do that is look at it by the parts. What is displayed there is three tools, x,y, and z. These are the averages for each part for that tool. In this plot, the average data, tool x is not reproducible compared to y and z. What do you expect that would do to the measurement process. This is an analysis of variance. Over the range of measurements, the ten parts they looked at, 83% of the variation that they were measuring was due to tools that were not reproducible. As you can see, 9% of variation was due to parts. They wound up replacing all those tools, with a different measuring technique and wound up with a level of 94% of all the variation was here. They did an excellent job of sorting out those parts.

When you do an interlaboratory study, you need to define how many labs will be involved in it, how many samples, replicates.

Pinoli   On the subject of replication, I have always had the feeling that 3 is minimum, actually 5 is minimum, 10 is better, 100 is even better.

Stone   No, it is 20, some say 30.

Kinchen   3 is an absolute minimum. 5 is a good number. Personally I would rather run 5 materials, 3 replicates on each than 3 materials, 5 replicates on each.

Stone
I would like to take you through a chemical sample. What we have here is a measurement obtained by two methods, the regular method and an alternate method. They ran 15 samples. If we take a look at this, both means are 10 and these are the standard deviations from method one and two and the correlation between those is 0.887. If you remember the intraclass correlation, what happens is an elliptical collection of points. They added four more samples and when they are plotted, this 95% probability ellipse, all are outliers. When you look at this as two separate methods and they are correlated, anything falling outside the ellipse is a problem to you. One of the ways to treat this is to go to something we call principle components analysis which is a translation of coordinate axes, mean set of the data, and as you subtract the mean of all the data from each one, that puts the mean at zero. You rotate the axes until one is lined up with the long axis of the ellipse and the other with the short. Given that coordinate system, you call that the first principle axis and the second principle axis and the projection of data points on these two axes are the values of those principle components. What does that do for you? One thing is that it uncorrelates them. They generate a new set of variables equal to the number of variables you had to start with. The total variances remain the same. Why go through this? It usually turns out that if you have a problem with 8 variables, you may find that only 3 of them, the new ones, account for just about everything.

Keith has some data that indicates that we may be able to do some discriminating. We are going to try that data and see. We may be able to go through a discriminant analysis which tries to come up with a function that will allow you to separate two groups of points.

We try and come up with a linear combination that gives us what we call a discriminant function giving us an optimal projection. We will see how this performs with Keith's data.

Fisher   I would like to welcome everyone to our campus.

Because a lot of you don't have familiarity with NMR, we do have a tour today at 3 and I think after you have seen the instrumentation, seen how sample handling goes, see how the computer operates, this will make it more real to you. We have recently gotten two new NMRs which have been recently delivered and just came up to specs last week. We gave the first two payments, which was over $1 million. We are very proud of this new facility. We have two 300 Mhz on which the data I will report on today have been done on. Even though the solid probe was delivered in January, it did not become operational until April. Even now one our transmitters is not up to snuff. We are just starting on our solid probe work.

We are using NMR to study phenolic resin and looking at the chemical composition all the way through the cure process, starting with the prepolymer and going up to prepreg and finally the composite. We are trying to look at the chemical nature all the way through that process. Another goal that we have is to use NMR to help confirm or not confirm other methods, like IR or whatever. We may even use NMR as a performance evaluator.

Today I will cover these items. I will start off with a short review to help you understand what I am doing and please stop me if you

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don't understand and I will try to go over what we are looking at. Carbon 13 NMR means that when we look at this, all we see is carbon. Everything else is transparent. Then we have the methylenes, they can either be an alcohol group or a cross linking CH$_2$. I haven't reported extracted prepreg before and I have my data on that now. I had to make a few more compounds, components that are actually in there and I will explain why. This expands my data base on what I needed to evaluate prepreg. We looked at three different extraction solvents and then we will give an analysis of both MX 4926 and FM 5939. Finally we are going to show some solids work that we have started.

In review of prepolymer prepreg, when I say Ipso, this is the term referring to the position of the constituent. It is the carbon that the OH is related to. Carbons occur at anywhere from 0 to 200 ppm and the aromatics on the left side, about 120 to about 160. The aliphatics are on the right side, about 30 up to 80. We have very wide separation of the types of carbon atoms that we have. These eight components are the major components of the prepolymer resin. This is SC 1008. Phenol itself is 158.2. That is this carbon and if you put this at the opposite position it goes to 157 and if you put it next door it goes to 156 and so forth as you can see. It is very nice because those are separated about 1 ppm. They are so nicely separated that these eight compounds can be evaluated very nicely as long as you have small molecules prepolymer. As you start cross linking and putting it together, you get more problems with it. You can couple together a couple of these, like 1 and 2 are 1 and 3. We have cross linked 2 of the phenols. These are alcohols, methylols, I call them. You will notice the difference

between where one is adjacent to the phenol, the ortho is at 61.8 and the para is at 64.5. We have several of these. We can tell whether the methylol is at ortho or para and we can tell the methylene is between an ortho and a para, para-para or ortho-ortho. I didn't find any ortho-ortho in this so I didn't put it on here. Those are not everything, but the major components that we have.

In looking at the region that is most important, the 160 to 150 region, here they are 1 through 6 and I put a standard in there. As you can see this region got a little cluttered.

This is SC 1008 and we have the actual prepolymer material that we are looking at here, and you can see the assignments of the compounds 1 through 6 and 7 and 8. That is the original numbers I have shown you where I made the pure compounds, I have separated and ran them so that I would know exactly where they were. Out in this range, it got a little more complicated. It was clear to me that even at this stage it was more complicated and I didn't have everything assigned. As you put more methylenes on, the Ipso position moves to the right. It gets more shielded, we say. Here are the ones that are more cross linked. You will notice particularly that this peak is not assigned and here we have an appreciable peak. Two big ones that we don't know yet. It was clear that we needed more information on the highly substituted phenolic positions that we have.

I wanted to have these compounds with methylol groups on them. Those are present in the mixture. They are formed normally by coupling, by crosslinking a couple of the molecules 1 through 8.

But instead of separating those, I started with this compound and prepared them from this reaction and separated them. I got at least 20 mg of each so we could get our spectra of the individual compound. There are five different products that you can have. You can put one on or two on, and this is what they are. On this slide I show you all five that I am talking about. The main thing that I am looking at is that 150 to 160 region again. We have these positions that come in. That is if you have an unsubstituted 4' Ipso position, 156.4, 154.3., 152.8, again because you are putting an ortho substituent, an ortho methylol will bring you approximately 2 ppm up field. We now have three positions, A, B and C.

Here are my new components of the mix that I have data on, especially the Ipso data. In like fashion, I looked at the other components the 2,4'. Now you get more products. There are 11 possible products in the reaction of formaldehyde in this phenolic. This makes separation a challenge and my student, Ping Chao, was able to isolate 8 of the 11. These 8 represent all of the types that we need. We have the entire type of substitution patterns that are needed from these components. Let's see what the results were.

Here we have the results of the Ipso carbons on the 2' ring. We have the types here that are necessary to evaluate prepreg. In summary on the next page, page 11, we have these types in the 4,4'. These are in about a 0.2 ppm range of each other. They all come in about the same range. These four down here are the 2' types that I just showed you. The next page shows you the actual numbers. these are the numbers for the Ipso carbons. I wanted to show here just how many examples we have of each type and how

close the ranges are. You will notice on the unsubstituted we have 6 of them and they are all very close.

These are the methylene carbons. I am not going to do anything with this, but we had the numbers and I will show it to you. These have smaller number values. These reinforce the knowledge that you have what you think you have, but there is not much diagnostic value in these.

Now in the evaluation of prepreg, in addition to the 8 components, I also have these 7 types. The data will be reported in terms of these 8 simple molecules and these 7 types of more complicated oligomers. This will help put this in perspective with what I showed you earlier. We now have these additional ranges and when I see peaks in each of these ranges, I can identify them. If I see peaks in other ranges, I cannot identify them.

We are now ready to analyze the prepreg. We have these major components, 1 through 8, and the major regions A through G. As we were extracting the prepreg, we thought maybe there were differences between the solvent used in extraction. Acetone was the tractional solvent used and we used that, but we tried some methanol and we thought at first that methanol was a little more efficient at extracting prepreg, taking resin out of the prepreg. We pursued that a little bit and we thought, well, maybe there is a difference. We saw different components coming out and we thought if it is starting to polymerize up, maybe the solvent is taking out different components. We looked at several examples of using IPA as the extraction solvent. You can see here that if you

don't have a little IPA in there, you can't separate well 7 and 8. These peaks here are very close together. Page 17 shows you the results. We took a series of MX 4926 prepreg samples and extracted them. We have a lot of different replications. This shows you the actual data for the solvents. I evaluated them individually and I couldn't see any differences of significance. Looking at the numbers between the acetone columns and the methanol, IPA columns, I couldn't see anything major. Down here, this gives me my Ipso region. and at the bottom is an evaluation of my methylene regions. Here is the FM 5939 reported in the same way. You can see the percentages for the first 8 components and the A through G components, as well as the methylene components. When I evaluate these and integrate these, I can integrate that entire 150 to 160 region. That shows me total phenolics. For the formaldehyde I have to add up all the methylene regions and they are much wider so it is more difficult to integrate. I integrate all these peaks here and add all of those up. I have a total for phenolics and a total for methylenes and then I ratio them. That is how this number is generated.

Here I am trying to evaluate the principal differences between these two prepreg samples. Without making a big amount of each component, the overview that I would have here is the cumulative values that I just summarized. By looking at these numbers, you can see that there is a lot less of these types of phenolics. We knew that and that is accounted for down here. That is the NMR analysis of the two prepreg samples.

This material is a solid resin that Tony sent me to study. It is just a pure resin sample and it was polymerized. I didn't show you this whole region here. These region that we can focus on is this region here. The 150 to 160 region is a little changed here. That is the region that I have been evaluating. In the solids this is what I get, just the nature of solid. This might could be improved slightly. There are some important things that we can see here. The Ipso phenolic is here and the aromatics are here. These are the metas. They are always unsubstituted. You have two metas for every phenolic. The orthos and paras that have methylenes on them also come in this region, but the orthos and paras without the substituent are over here, 116 and 121. This is how much methylol we have left. Here is a little IPA. This is a broad region of what you see.

Bhe   Tony, what kind of resin is this?

Day   This is SC 1008. It is from the same batch, in fact, from the same can as all the previous specimens that have been sent to Tom. I just cured this in a mold, neat, at Marshall and I think I set platens at 350 and I held it until it would hold pressure and then I took it 1000 psi and left it for 2 hours. It is a plug, about 1½" diameter and about 3-4" long. We cut it up and sent some to Tom.

Thomas   If you take the chemistry of these two resins apart, can you say one should wet out a fabric easier, better, more uniformly, or one should cure better in an autoclave or hydroclave process? Is that the end goal of something like this?

Fisher	What I would really like to see, and I haven't done yet, is a sample of cured 91LD. That would tell me an awful lot if I knew how much amine is left here, in addition to the methylol. Is there any amine left in the cure process.
Thomas	Certainly, you are pointing out the differences in trying to understand what the differences mean and their contribution to the process.
Upton	That is where we come in. Tom is not as much a part of the process as you are. Pretty soon this will all click in our mind and this make a difference with what we do with your knowledge of the process.
Day	I don't think we can make much of this for the process. That would depend upon his measurements. It does give us some insight as to what is cure and how far do you go. We actually have a method now of comparing two different solid material. If one doesn't cure as much as the other, we can see it. We may have a tool to be able to tell the difference between a postcured and a regular cured phenolic, or evaluate the difference in curing at 350 versus 310.
Upton	The IPA content is still a question. We still don't know where that is coming from and we may find in the future when we run more of these solids samples, we will see more of the IPA.
Day	Yes. Those are questions that we have always had. We have seen a lot of strange things in phenolics, but because we don't know

much about the nature of the cured material, maybe this is a way of getting a handle on it.

Thomas   Cindy, is the end goal to get a chart like this one on SC 1008 for 91 LD and on down the line.

Upton   Pretty much. Tony has already done the same kind of background work that he showed you for SC 1008 on 91 LD. He is basically building his own library and he can tell you anything you want to know about it from his library of data and from running his samples. We will have an unprecedented level of detail of our material. It may be hard for us to sort it all out, but I think we will be able to. You know we haven't even started cure studies. We need suggestions on that type of study.

Day   What we have been waiting on is solid probe.

Upton   Yes. Tom could go just past gel point. I am very encouraged because this is Tom's first shot at solids and now we know about this region up here. I think that is very exciting for a first run.

Day   It is confirmation of the IPA which probably says that the resin is trapping the IPA. At 350°, there shouldn't be any IPA.

Bhe   You might try to run the glass transition temperatures, DSC and correlate with this.

Day   DSC scans of this material is typically flat.

Upton	We just do prepreg, but there be another method we could do to correlate the information.
Fisher	I have one more slide here. This is an aft cone, material number 120, and the spin rates here, I had to go to 12 Khz. That is pretty fast. One of the problems that I had with the composite material that had all the carbon in it, the way I handled these was I had, well Tony ground these for me. I have a blender, but my blender is too big to powder this up. The problem was I got arcing which means that I had such high voltage across there it was sparking in the sample. I had to turn that way down. With the one-fourth detail I have shown, I ran it again, that is the pure resin, and the same power and got about the same thing. I know that if I can get around the problem of arcing, that I can get the quality of this one nearer to the quality of the other. I think we can get similar quality out of this. We don't have good data here yet, but I am hoping that we can in some future work.
Pinoli	Tony, would it be appropriate to get some machine dust to better represent?
Day	That is what we did. We make a lot of that.
Pinoli	Thank you, Tom. I think we will take a little break here and come back in about 10 minutes.
	I have asked Bob Shaver to talk about some test work that we have done in his area and I will give you some background on some work that we have done at Lockheed. What I had in mind here was an

overview of the highlights. I am not prepared to go into depth about a whole lot, but I think there are a lot of points that are worthy of talking about because to me there are some very complex features of the carbon microballoons. That is a very complex product. Along with complexity is a very limited number of acceptance tests that are performed. While this product could go out of control very easily if someone wasn't protecting us, in reality, it is behaving very uniformly and has done a very good job. I think at the conclusion of the program, which was the Pathfinder phase of the activity, everybody is getting more and more comfortable with the LDC product. We are looking forward to continuing the program and introducing the product into the ASRM program. With that as part of the overview, I'll take the first portion of the presentation with regards to the objectives of the program.

As part of the FM 5939 LDC Optimization program, we were tasked to do a comprehensive study of constituents. As a followup of the program, we went on and looked at Type A versus Type T carbon microballoon properties. The difference between A and T is that the entire DOD data base on LDC is based on Type A product. In our ultimate wisdom we introduced the Type T for the ASRM program. Management continually looked over our shoulders and asked why we wanted to do that. They wanted to be shown why the Type T is the better product. The results of the activity pretty much confirm that our decision was right in introducing the Type T into the program. There was nothing that came out of the initial Pathfinder study that suggested that Type T had some aspect that could introduce variability or an inferior

product. Rather than dwell too much on the carbon fabric, I will simply throw up the conclusions that came out of the final report. That was that we looked at the surface condition of the CCA8+ product and found it to be consistent with the rayon based carbon fibers, particularly those that are used in the RSRM program. XPS surface analysis showed the presence of substantial amounts of oxygen and confirming that it is an activated carbon and a slight amount of sodium showed up. This is what we expected. Surface area measurements were right in line with what we expected also. The CCA8+ fell exactly where you would hope it would fall on the air oxidation sensitivity, which is a SPIP developed test. The oxidation resistance is a little bit better than the current product. There was no indication that sodium was showing a catalytic action. Moisture adsorption was a little bit down from the level which you see in the RSRM product, but it fell right in where we expected it to fall. The net result was that it looked good. It looked uniform.

The work that we did at Lockheed gave us, myself in particular, an opportunity to look at carbon black. Both BP Chemicals and Lockheed looked at it and said that yes, it was carbon black. It was very small, submicron, clumpy. XPS surface analysis also showed a little evidence of oxygen on the surface and that was to be expected because it is slightly hydroscopic. The firing temperature suggests that it is just at that razor's edge of activated carbon. Surface area numbers as I recall came out to about 35 and that suggests that there is a little bit of internal porosity. Oxidation sensitivity was something that had never been tested before and I will show some data on that when we get into the carbon microballoons. They look very favorable, better than the carbon

fabric. Moisture adsorption testing showed just a slight amount of moisture adsorption. Apparent density is a packed density. That came out where it is supposed to be and the apparent stiffness is a test that is routinely run on carbon black and it was normally what you would expect to see.

Now we get into the carbon microballoons and I am going to ask Bob Shaver to come on up.

Shaver   The situation that we were addressing is that the Type A carbospheres, carbospheres being a trade name, are a material that has been sold by the organization that I represent for quite a number of years under specification that we basically generated ourselves to, among others, DOD contractors that were making apparently LDC material for use that was similar to what was contemplated on the ASRM. It is not the only use for the material, but it was a salient one and it went on for quite some time. When the ASRM project came along, the idea was to translate to DOD technology into the ASRM situation, which is a larger nozzle and a man-rated product. Those people involved, some of whom are here, came to the common sensical conclusion that the sodium content of the material which was fairly high compare to the other constituents in the ASRM nozzles and common sensically it should be reduced and improved. A common sense idea, but not demonstrated. I was asked to produce a variant of Type A which was a higher purity material. The impurity of Type A was a form of oxidized sodium, principally sodium carbonate. It made sense that the reduction of that impurity would benefit the outcome of the rocket nozzle when exposed to high temperature. A proportion of the normal

production of Type A had a low enough ash content to have sodium content within a range that was being talked about, ash content at less than 1%. We believed that this was possible to do on a consistent basis.

Pinoli   I don't think you should have to defend the decision to go to the low ash content. That was based on recommendations, one from myself, that I have never seen any attribute that was favorable in hav . an ash content, high sodium, in an ablative application. Tha. :alls back into the fiber activity that we did early. We looked heavily into the sodium content and the only rationale that I could use that was defensible, was that I had never seen any positive advantage to have sodium there. I could see negatives coming out of the oxidation behavior, so the decision to go to higher purity made a lot of sense.

Shaver   This slide shows that the only significant difference in the way that we qualify the material was in the ash content. Here there is a 4% max and in the Type T, a 1% max.

Hill   How did you get the T? Did you select it from a batch that was made?

Shaver   No. That was one option, to make a lot of A and select out the minority that would fall in the T range. That didn't seem to make any economic sense, so, basically, we tightened the processing parameters that we used for our normal range to yield material in that range. A large portion processing operation is directed at control of that particular constituent, the ash constituent. It can

come out of the product stream at a very high level, much higher than we are talking about here. We do a lot of removal of ash in the normal process stream in Type A.

These SEMs are not in the handout, but they are pretty pictures. This is a very complex material. All microsphere particulate materials tend to be complex because they are so many of them in a small sample. The carbon microballoon is a carbon analog, in a simplistic way, of the glass microballoon or plastic microballoon. From my point of view, the major differences that we are talking about is carbon, a ceramic friable material, whereas the glass or plastic are vitreous material and therefore have different characteristics. For those of you who are familiar with glass microballoons, you will recognize, when you do an SEM, mostly what you see are microballoons that look round or roundish. You see very little of anomalous structures that are angular or crystalline looking structures because it is vitreous material. If you destroy some of the microballoons, you do see some structures that look like this. It is difficult to produce a quantity of microballoons and not have some that look like this due to activities that go on, insults that occur. They all tend to do some kind of damage to the microballoons

Microscopists don't like to look at the usual things, or the average things. They like to zoom in on the unusual and the grotesque and what not. These nests of microballoons are there, too. They are a substantial part of the whole thing. From the point of view of understanding what the material is, it is sort of like astronomy. It

is better to have a wide field. This is more representative of what carbon microspheres are.

Pinoli

I don't know if you can ever assess what is going on inside that. These are little balloons that are semi-bonded and clumped and getting a sieve analysis is not really going to tell you what that is. It is very difficult and complex to analyze.

Shaver

This gets back to the process. The material is made from a carbonaceous precursor and, in so doing, there are solid states and gas phase transport reactions that go on at high temperature and they do tend to do all those things like bonding together. When the process isn't done right, they are bonded together very strongly and you have something that you with you didn't have because you either have to throw them away or you have to apply a biomechanical action on them to break them apart. They may break where they will and not necessarily where you want them to. In process you try to avoid that. As Pat pointed out, groups that look like agglomerations are physically bonded. It is not possible to look at the SEM and prove that, but it is probably true. The final step in our processing is passing the material through a 200 mesh sieve. It is possible that there would be an agglomerate that size.

This particular microballoon shows a lot that is interesting. The major thing is the surface texture. This is a common characteristic of the carbon microballoon that we made of this type. Not all of them have that surface texture, but most of them do. I have no explanation for why they don't all fall one way or the other. Even on this there are areas that seem to have no surface texture, areas

that have little, and areas that have a lot. That is all I can say about that, it is characteristic. Everything else that I would say is conjecture. I believe that this has less surface texture than this because in processing this was at a place where another microballoon was lying close to it and blinded it from whatever was going on. I believe that this one was bonded and perhaps it was broken off in the sieving process. Those are fairly common things to see. You can ask yourself how can you make the carbon microballoon outgas. The process does not take place over infinitely long periods, so there has to be some relatively gross gas flow going on in these things. Certainly these kind of holes facilitate that. When we do density testing of these materials, one of the characteristics is that using a liquid picnometer versus a gas picnometer, you will get quite different results. The gas will give you an apparent higher density than the liquid will. Furthermore, the gas will give you a value, depending on how you carry out the test, that will vary with time. It gives you the impression that gas is diffusing in on the time scale of minutes through holes that are the appropriate size for that to happen. This happens to us all the time.

Pinoli   One of the things that I found is if you take these microballoons and try to dry them out and place them into a beaker, put them into a vacuum oven at about 110°, the thing that struck me as weird was that they would have a tendency to start jumping out of the beaker. The first thing you knew, they were all over the vacuum oven. It is literally due to the outgassing. It is a very, very active product.

Shaver	This is just a mess of numbers meant to say that after we produced 5000 pounds of Type T, we compared the measured data base of qualification tests to our data base of the Type A that we have generated over the years and we found that with the exception of the ash content and the other non-specified parameter of moisture adsorption, which we believe is related to the ash content, everything was statistically the same as Type A.

Th the graphical distribution of the Type A database that hopefully stops at 4%, but averages around 2% for the material that we have made over the years, about 20,000 pounds. The Type T that we made had this distribution, over about 5000 pounds. I don't know that we can attribute anything to this. Personally I don't see any reason to attribute anything to it. We did what we had to in the process to limit the ash to 1% which we in fact did. We did not have to reject or throw out any material because it slipped over. We were able to control the process and everything that we made as Type T wound up as Type T.

The next slide in Pat's handout here is the relationship of ash in carbon microballoons and carbon fabric.

Pinoli	The reason that I threw that one in, Bob, is to try to point out the significance of what we found on the program. I looked at the carbon fabric from the standpoint of the relationship of ash content to sodium and you wouldn't necessarily associate the carbon microballoon data on that relationship to carbon fabric. There has been a technical rationale as to why these two are the same and that is the form of carbon, the form of sodium that we have is identical,

both in the carbon microballoon and the fabric. The database down in this region, for carbon fabric is quite high. There is a tremendous amount of data. I have just shown two data points, but it is an excellent relationship developed by a considerable amount of data. It is much simpler to measure an ash content than going as far as measuring sodium, so we have a good solid relationship, and it is nice to extend this all the way out to the carbon microballoon.

Shaver

This is that other parameter that I was referring to, the so-called moisture adsorption. It is not a parameter that we have a historical database on. It didn't exist prior to 1990. We do have some information on all of the Type T material that has been produced and some of the Type A that you see here. It is a relatively small amount of A. It was not a major effort during that time period. What we see is perfectly consistent with the lower ash content in the Type T than in the Type A. The curves are displaced towards lower moisture adsorption. That is the sodium oxide carbonating whatever, the ash constituent being hydroscopic. This test was 24 hours, 100% relative humidity.

Now we come to Arrhenius plots which I would be happy to talk about, but I am sure that Pat would be unhappy, so I yield to him.

Pinoli

The thing that I liked about this data is that we looked at the spread where we had data on Type A product. The plots that you see here represent the wide distribution of oxidation behavior we had reported for Type A. The way to read this is that this is oxidation rate. This is mass loss rate versus 1/T. To make it simpler, we put the temperature in ° C up here. If you want to compare behavior

at 400°, you can see that you are at 10^1 at this point and drop down to this point and you have a much lower oxidation mass loss rate and comparably as you go lower and lower on the charts, it is a very significant reduction in the oxidation mass loss rate. The favorable direction is to move these curves closer to your baseline product which is carbon fabric CCA8+. This is where we have an extensive database on CCA3. It should be somewhere in this neighborhood. Logic would dictate that this product is behaving quite well. We are trying to get the product to move to the more resistant direction, which is the carbon black filler which is extremely resistant to oxidation. To get back to the carbon microballoons, we also tested a number of lots of Type T to get a feel for where we were and you can see that these two products shifted in the positive direction, behaving as we would expect. What was missing from this entire analysis was the catalytic action of sodium. Typically the carbon fiber as you approach around 2000 ppm sodium, you begin to develop a knee in the action, somewhere at about 500°C. It tends to break off at a very high rate. This was very profound and sort of identified the underfired fiber. I fully expected to see the same type of thing on carbon microballoons, but the last of that knee in the oxidation behavior was so consistent in all the data that we developed that you had to stand back and say that there had to be a rationale for that. The original rationale that I came up with was that the sodium may be trapped in the microballoon, not accessible to the oxidation process. That would deplete the oxidation inside the microballoon very quickly and therefore, would not influence this oxidation mass loss. That would mask the effect of the catalytic action.

We did a series of experiments where we ground the product up to release that sodium to see if we could see some changes in the product. That brings us into the surface area measurements and here we begin to see the ground product which is almost a dust particle size. This is as-received product and this is ground product. We looked at the Type A and in this case we are looking for surface area variations. Frankly when it comes to grinding a product up as opposed to as-received, intuitively you would think that you are significantly increasing the surface area, but in reality the type of numbers that we are talking about here really don't contribute that much. I would have been surprised to see a significant change. In this particular instance, you can see that it did not increase, but went down a little bit. The same effect happened on the Type T with one exception. Here is seemed to go up. Comparing the two products, the nitrogen adsorbate data looked about the same, and the CO_2 data, which is designed for activated carbon, shows significant differences with the nitrogen adsorption. Some of these are about a 50% increase which confirms that we are dealing with activated carbon. This was the outlier that was interesting to Corky. 209 is a significant number. One of things that is missing here is that we don't know what the spread is and you have to do an awful lot of testing. It could be that the spread is somewhere in the neighborhood of 200-3000 versus 64. I didn't draw any significant conclusion to that, but Corky insisted that we go back and take a look at that product and I never documented it in the final report, but you can see from the SEM photographs of that lot that the higher surface area could be accountable by the possibility of air oxidation. The product had been exposed to some air oxidation. The way you identify that is

with SEM and look for pitting action that attacks the product. We agreed that what could have happened was that it came out of the furnace a little hot and a little bit of oxidation occurred. It gave us some insight into what could happen.

The other significant thing that we spent a lot of time on was the surface analysis of the carbon microballoons. I thought that I would quickly go through some of these and present some of the work that was done by BP Chemicals. Donald's work with the XPS back at Warrensville confirms that we had oxygen on the surface. It showed a considerable amount of sodium that was believable, a little sulfur and some chlorine. I feel very comfortable with these numbers. Nothing is too much of a surprise here, but then Donald and Warrensville got actively involved in some Auger experiments. Auger can be run on very small plot sizes. You can do analysis in selected regions and look at flake areas versus non-flake, areas that were devoid of flakes, nice, clean billiard ball type of balloons. Just to give you a little flavor for what he was finding was that he took an area to be very low sodium, no flakes and he took an area that was heavily concentrated with sodium. Likewise he took the interior of a broken microballoon and looked at the flake area and no flake area and this is where we came into a lot of disagreement. The original interpretation was that this was confirmation that sodium is directly associated with flake regions. If you look at a billiard ball surface, it is strictly carbon, but if you look at this flake region and you see sodium. You can't discount that kind of data. Also he took a series and in this case you begin to see the complexity of this whole thing.

One side issue that I felt was significant was the issue of where the sodium is, inside the microballoon or not. We ground the product up and we did more than just grind it. We actually took the as-received product with ash levels in this range, 0.64-0.59 with comparable sodium levels in ppm and ground the product up and sent it back to Bob for purification which is not intrusive, but the thought was that by exposing the internal surface, the purification process should remove any of the trapped sodium that is inside the microballoon. My real hope when we did this simple operation was that these numbers would go down to zero. We had the opportunity to get what was trapped inside the microballoon. The net result was not too positive, really. This came out rather on the negative side. We got it down a little bit, but it wasn't what we hoped for.

We brought the sample back and did an acid wash with HCl to see how effective that would be on the ground product. Lo and behold, we saw these results. The acid really does a super job getting rid of the sodium and so the logic there was if that was the case then go back to the as-received product and acid wash it and by acid washing the product, we found that we could really knock down the sodium levels to around 200-1200 ppm. If we want a really ultra-pure product, I think we came up with an idea for doing it that will not significantly alter the product itself or its behavior in this application.

Now this next thing, organic liquid properties, this was your baby, Bob.

Shaver   The idea here was to, since our material is complex and you can't really visualize the material, to find out interesting things about the material by doing dispersions in various liquids. The common sense thing that is a material has a particle density of around 0.4 grams per gc on the average, that material would float on most common liquids, most common liquids being heavier than that. And in fact, if you take the material and throw it on water or whatever, most of them float and some of them sink. The question is what is going on here.

Part of the answer is perfectly obvious to anyone who thinks about it, being as diverse a material as it is. Some of them are larger, some of them are smaller. It is a fact that for all microballoons that I have ever seen, including the carbon microballoons, that the smaller ones have a smaller particle density. There is no ultimate scientific reason why it has to be that way, but apparently it is an artifact of the way they are made. Some relatively uniform amount of mass is blown to smaller and larger balloons. That is a gross assumption, but it is a fairly accurate model of what must be going on because the smaller ones are always denser and they are significantly denser. Some of them are going to be small enough that they are going to be dense enough to sink in some liquids. The other thing that you see is that the broken material is more or less likely to sink because it is truly carbon and it is going to have a density considerably above 1.0, 1.5., maybe 1.9. In most of the liquids that we were talking about, a broken microsphere that is thoroughly wet out by liquid should sink. That was the presumption in the most simple model that we could think of when we performed these tests. Some of the numbers that you see up

here are logical in the face of that model and some which blew our minds.

For example, the most dense liquid that we had, carbon tetrachloride, had the lowest amount of sinkers. We measured the volume of the material before it was exposed to the liquid and took off the sinkers and measured them by volume. The densest liquid had the least amount of sinkers. This was very logical. The least dense liquid, hexane, however, although it had more sinkers than the carbon tetrachloride, it was far, far away from having the most sinkers. That is where the simple model started coming apart. We did the obvious things. We looked at the characteristics of the liquid and we are looking for surface tension effects which can be seen where low surface tension does not help us here, it obviously did help in ethyl ether. That was the liquid that sank the most. We had confirmation in one sense and confusion in the other sense. The other characteristic that seemed to be a significant determinant of the behavior of the material in the liquid was the degree of polarity in the liquid. The ones that were more polar did a better job. In fact, there is a group of liquids that we consider to be good candidates for dispersion tests. These are isopropanol, methanol, and acetone. These have a reasonable density and some polarity. They seem to act pretty much the same.

The test that we did do on the Type T microspheres to assess the sink/float was the methanol. That test was to take a measure volume of microspheres and suspend in methanol in a graduated centrifuge cylinder and centrifuge for a standard amount of time and

then read the amount of sinkers and that is the volume fraction that we reported.

Pinoli

This is the one thing that did seem to make a little bit of sense. When we lined them up, everything is grouped as the % sinkers and this was a judgement call. There was very low, low, intermediate and then high % in ethyl ether. The relationship to liquid density looked solid with the exception of hexane. That was the outlier. Everything else seems to be in the same general trend. The liquid densities are all about the same here.

What I was trying to get out of this was the intrudeability factor of carbon microballoons. If the product is changing with respect to that intrudeability, then how can you expect to control the density of the product. If it cannot be measured or controlled, all those parameters blow up. However, your product has been extremely consistent. I think that this methanol test is doing a pretty good job.

Shaver

That is a test that we have a large database on. We have been using it on another product that we have been making in very large quantity over a number of years. We have used this as a sort of process control, accept/reject sort of thing to be careful that we weren't damaging material in the process. It seemed to make sense from the point of view of what Pat is looking at, intrudeability.

Pinoli

From the acceptance test point of view between A and T, Bob likes to view Type T as a subset of Type A.

Shaver   From our point of view, what we measure we will be seeing as a subset. My editorial comment is that we haven't been able to see that reflected in performance. We haven't been able to get any performance data.

Pinoli   I feel that we are on the right track.

Hill   Did I hear you say that there is no performance data on Type T?

Pinoli   We haven't fired...

Hill   We fired in the SPIP 3 nozzle with Type T and Type A. They looked the same.

Shaver   My personal reaction to that is that I am not surprised.

Pinoli   I want to briefly go over some of the Karl Fischer study we did for the Pathfinder program on prepreg. We ran three different formulations and what we were doing is varying elastomer content and microballoon content. Carbon black remained constant and resin and fabric varied a little bit. The Karl Fischer analysis looked at water so you have to look at resin content a little bit and get a feel for the fact that if you have a higher resin content, you would expect a higher moisture content. Here is a little bit of data regarding inhouse testing of those panels. There were significant differences with regard to shear properties. Run number 15-2 seemed to have the optimum shear strength.

C-2.

What I tried to do with Karl Fischer was measure the amount of moisture that evolved from the product during the cure, and what I tried to do is develop a material balance to track the resin in to the premix, into the prepreg, and then into the composite.

This analysis shows that there is almost a 1 and 1 relationship to the moisture content measured in the prepreg to the final product. What that says is that the typical cure processes that we employ do not remove any of the moisture from the composite. It is simply trapped. What you go in with is essentially what you come out with as far as water content.

Here as you can see, at 325 the cure of 91 LD, water released was 13.1% and at 12.9% at 500. There is some additional crosslinking occurring in during the higher temperature cure. You have to look at standard deviation in your results and say that is not really significant. There isn't a ½% or 1% difference that shows up in the composite. The fact that in the premix, you see the same general relationship gave me confidence that the work was trying to tell us something and that was if the moisture can get out readily, the water measurement at these two temperatures are identical. The other thing that I wanted to assess was the amount of moisture that was released with respect to the quantity of resin that is in the premix. Your numbers should diminish. I was relatively happy with that and I was happy with these numbers out here, which is the water ratio because you are highly solvinated in these conditions as opposed to these conditions. Here you are still highly solvinated but you also have the filler, so the percentage of water in total vols is coming down a little bit.

Bhe   What kind of ratio is that?

Pinoli   That is water ratio to the total mass loss. Moving on to the
                           prepreg, there were ½" diameter disks, 3 for each one of the ones
                           that were performed. A disk that is bored out of prepreg that is
                           only ½" in diameter is not an awful lot of surface area. The
                           concentration of resin varies considerable from one side to the
                           other. The fabric picks up resin with respect to the wettability of
                           the fabric. It is controlled by characteristics of the fabric and so
                           subtle variations in the fabric are going to strongly affect the
                           variability of resin concentration on the prepreg. By sampling such
                           a small unit, realistically, you should expect quite a bit of variation
                           in the water content. Indeed, that does show up in the data.
                           Weight percent here of 4.21% water is pretty much confirmed by
                           looking at the total weight loss and the percentage. All the
                           percentages stay pretty close. When they don't, you know you have
                           an outlier. There is confirmation here of what is going on in
                           sample variability and when you run into a case like 3.09 or 4.16,
                           well the resin is not uniformly distributed and you have a problem.
                           The only way to use this techniques effectively is to increase the
                           sample size, however, the device limits you in the amount of water
                           that you can measure. That brings us to the composite.

                           A few surprises showed up as far as the water concentration levels
                           are concerned   First off the water content is extremely low.
                           Traditionally we don't see numbers like this, 1% water. The vols
                           content was fairly consistent, but every once in a while, you would
                           get a funny one, like 4.20, 2.9, and I think that what this was really
                           telling us is that there is a considerable amount of variation in the

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panels that we were manufacturing. The more we studied the uniformity of the panels, we realized that each one of these panels was not a consistent product. It was reflecting the preform conditions that were incorporated into the way we made the final panel. Depending on where you sampled within any particular panel, you are talking about variability. The other thing that was obvious to me was in order to get such low numbers on water, the cure cycle had to be very effective. We were drawing down the water content considerably, so that means during cure we were able to pump out a lot of the water from the composite that we normally saw. In an LDC product, that is probably very favorable. If you look at other data from the standpoint of LDC, you saw very high numbers in moisture content. We never went beyond this point and if you are going to use the product in the future, you must be extremely careful.

Thomas   Pat, can you say that microballoons have a tendency to absorb water?

Pinoli   I think there is no question about it.

Thomas   Might that be where the water is going?

Pinoli   It could be hidden, but the Karl Fischer would show it up. At this point in the game trying to understand why LDC works and doesn't work isn't clear to me.

Thomas   Is that an additional contribution to the plylift?

Pinoli   Yes, it could very well be.

On the conclusions, Don had heartburn that I had this 60% resin solids in 91LD up here. His 91 LD had 70% resin solids. I had to draw the conclusion based on the data that there wasn't additional cross linking occurring significantly that we could see to suggest that the 325 and the 500 produced different water contents. The fact is that if you are going to run prepreg, you have to increase your sample size because we are not getting sufficient quantities based on the small area that we are testing. Residual vols in the panels was extremely variable because of the preform construction and that has to be addressed if we go back into this program. It turns out, I think that our Pathfinder program was degraded to a study of how to make panels as opposed to how to make parts and residual vol measurements, I thought the Karl Fischer data gave a lot of insight as to what was going on. I think there is a possibility of getting that performance related test out of that.

Recommendations for the program, we remain lacking in a test measurement for intrudeability. We are on the right track for the sink/float test. We need to perform a heat treatment study to find out how sensitive the carbon product was and what effect those carbon product variations would have on composite properties and performance. We have to develop a test method for particle size distribution. As I indicated, it is an extremely complex product. Traditional methods cannot be used. This is a tough one. We have no background on particle size distribution on composite properties and performance. We would also recommend that the Karl Fischer be followed up to see if we can get a performance related

acceptance test. That pretty much wraps up where I think we left off with LDC, waiting for the next generation to pick up.

Thomas

Pat, does this conclude your LDC testing with the ASRM cancelled?

Pinoli

Yes. There has been no indication that RSRM is going to pick up on this at the present time. I have a thought process that it is ultimately going to be back as part of the improved version. I thought we were beginning to make good progress on the product. We were getting more comfortable with it. I know that the team members of Thiokol were almost believers.

Let's pick up with Tony and the carbon sulfur study. Tony and I are going to handle that.

Day

Last year in the chemical literature, Thermo-Jarrel-Ash came out with a Multi-Element method that they claimed would be a great way to fingerprint for cure. Basically it is a simultaneously multi-element inductively coupled plasma which is basically an upbeat form of the atomic adsorption method for doing elemental analysis. The good thing about it was that you could do a whole bunch of elements simultaneously. I called them and they said that they would be willing to run a free specimen just to try the technique.

While we were there, they ran a DC arc spectrograph of a forward tag end and the primary thing that came out of this was they couldn't quantify to well, but the thing that popped out was that we had a sulfur level of 120x the background. I thought, how could

we have sulfur. That is not one of our problems. They carried on with their analysis and they scanned all of these elements and they got this 120x background sulfur again but it couldn't be quantified because of the matrix. We have a lot of carbon.

Bhe What is the objective of studying sulfur?

Day That is what I am telling you. Anyway, what we found is that with this method you have an interference from the reaction between carbon and nitrogen. The carbon reacts with the nitrogen in the air and forms a cyanogen reaction and really makes it difficult to quantify the regions where you look for sulfur. We decided to run this multi-element simultaneous ICP so that we could get an accurate number. It turns out that you can't get it on that either, so we just did it on standard ICP, which is a real good way of performing a sulfur analysis.

This is the data that we got from them and as you can see that there is very little in the SC 1008. We were looking at this as a way to do fingerprinting, so that doesn't seem to be a good way to fingerprint. It probably is not a real great way to do the composite either.

Looney Tony, what does BDL mean?

Day Below detection level.

There is a little lead, but not much else. We ran standard ICP on sulfur and it is definitely there. We ground up the specimen and

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extracted it nitric acid. We ran the SC 1008 and the S/N 111 and sulfur is absolutely, definitely there. We ran a 1 to 100 dilution and it came out at 706.8 ppm in the S/N 111. There is no sulfur in SC 1008. They estimate that this about 50% recovery factor. They didn't do extensive extraction on this. With that estimation, 1413 ppm of sulfur, which is way more sulfur than we normally have in carbon, or composites. So I presented this to Pat.

Pinoli   Now I get to answer why we are doing this. When all else fails, at the last minute you are forced to go back to the literature and recognize your shortcomings.

There is no question that sulfur is a puffing agent in the manufacturing process, but as Tom Paral has put it there are times when you introduce sulfur into graphite because it does promote other facets in the production of graphite that are favorable. The favorable attributes from the graphite standpoint is it generally tends to promote graphitization, if graphitization is favorable and you want high conductivity. It has been shown on some studies to increase char yield. The way they work with sulfur is they combine it with inhibitor, iron oxide and they control the puffing action which supposedly releases H_2S. At this stage of the game, I am not too interested in specifics of that. It doesn't traditionally come out until it is heated at 1400°C to 1800°C. While those temperatures are a little bit above where we fire the rayon fabric, such that you would expect that if the product had sulfur to start with, chances are there are some that is left over in carbon after firing. It is a stable form of carbon that you traditionally wouldn't

think would cause you any problems. It would be stable up until you reach this point.

Bhe   Does the sulfur actually exist by itself?

Pinoli   It is functionally bound to the carbon lattice structure. The reason that it comes out as H_2S is there is always a certain quantity of hydrogen left. Those two could react and could come out as a gas and what it forces you to do in crystalline graphite is go slowly through this temperature range, so that the evolutions are slow enough. As the heating rate increases, the influence and the explosive nature of the outgas could be very significant. You generally try to avoid this condition. Also there is a cost parameter that comes in . Anytime you slow down the process to go through this critical range, it will cost you money. The thing that really intrigued me is that this looks similar to the dynamic TMA data where we showed the effect of water, the dynamic heating rate had on the across ply expansion of the composite. You could almost overlay this to work that was done along those lines. The only big difference is that it is occurring way out in the 1500°C range. If you are concerned about ply lift, you have to look at this and ask if there is some reason to believe that sulfur could be a contributing factor in the char zone or is a possibility that if there is sulfur in the fiber, it could be counter-reacting with outgassing products at low temperature such that this event is being shifted to a much lower temperature.

In order to further investigate this, what we did was samples of conventional carbon fabric, CCA3 and CSA, underfired 10B,

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overfired CCA12, 2 PAN representing Amoco 25XAB and Hercules LF-2, 4926 prepreg, S/N 111, one with Type A and one with Type T microballoons and also threw in some Shawinigan carbon black filler. These were sent to LECO for analysis and the net results are shown here.

There is a slight variation between the CCA3 and the CSA. I don't draw any conclusions from that. We are looking at a ball park range. The fabric was in a pretty high range. CCA12 was in the same ball park.

Paral   Pat, these are LECO numbers?

Pinoli   Yes. I have no way to compare them. How do they compare with your data, Tom?

Paral   They are a little bit higher, but historically the fibers we measured are slightly higher fired than that. I can't recall right hand the numbers that we have on fabric. I will get you some dback on that.

Pinoli   Great. Obviously we are not in a position, at this point, to talk about current production. I know this CSA product is an Avtex product. It is about 5 years old. What I really want to do is look at North American and compare it with Avtex. My experience on the North American product has shown that their rayon is traditionally lower in impurity levels and is more consistent than Avtex ever was. I would expect slightly lower numbers from the North American.

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With regards to the PAN, as expected, there are very low sulfur numbers. The prepreg is showing a pretty high number. This surprises me a little bit. It would suggest that the filler is bringing in some of that. Likewise these numbers for S/N 111 are holding up. Carbon microballoons, as expected, did show significant quantities and the carbon black filler was almost insignificant. They made five tests on this and it kept changing on them. That is not inconsistent with carbon black filler. The impurities seem to be agglomerated into regions, so everytime you test, you get a different result. That spread is indicative of that.

Paral   Is that a gas black or an oil black?

Pinoli   I am going to say oil.

Paral   Historically, black was made by using oil. The newer ones are made burning gas in a lack of oxygen and are quite different in sulfur content.

Pinoli   I would expect that.

Paral   We had our own black process for years and years. Most new ones are now gas blacks.

Pinoli   Acetylene or natural gas.

Paral   Yes.

Pinoli   Tony, do you know whether it is oil or gas based?

Day   I do not know.

Pinoli   The obvious source of the sulfur goes back to viscose rayon. We
                       all recognize this. There are no surprises here. We have a
                       maximum limit of 0.25 weight percent in the specification
                       requirement. I just received some data on Avtex and Bob has
                       volunteered some data on the North American product. We have
                       a chance to look at those two products and try and get a better
                       handle on whether the current product is cleaner with regard to that
                       or any different from the Avtex.

                       For those people who are not truly conversant on ppm and weight
                       percent, I have a very simplistic chart to give you a handle on what
                       we are talking about. If we start out with the sulfur level in rayon
                       of 0.10 wt.%, with a carbon yield factor and using a 5:1 ratio,
                       then you could expect 5000 ppm, or if you use 22.5 % which I
                       think is a better average for yield content, you could say that all of
                       the sulfur that was there at 0.10 wt.% came through to the end
                       product. You could say that it relates to 4500 ppm. Likewise, if
                       your yield was 4:1, then you are down to 4000 ppm.

                       Sulfur can be trapped in the cellulose structure in a number of
                       ways. It can be xanthated with sodium sulfur, an organic form of
                       sulfur. It can be inorganic, trapped sodium sulfate. Likewise you
                       could end up with sulfur in a zinc xanthate and zinc sulfate. Those
                       four possibilities exist. I always thought it would be interesting to
                       identify what form of sulfur was in the final product.

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Current test methods for measuring sulfur in rayon, this is heartburn city for any chemist these days, goes back to liquid chemistry. We produced a barium sulfate precipitate by burn off and it proposes to measure both the inorganic form of sulfate and the free sulfur which is tied up in the lattice structure of the cellulose. Tony and I have been batting this back and forth, and we are not sure whether the test technique is capable of picking up all of the sulfur be a reactive process which is nitric acid and the HCl. That is designed specifically to break down the organic structure of the cellulose.

Day
Typically what they do with the rayon is dissolve a sample in the mix of nitric and hydrochloric acids and that destroys the organic nature. Hopefully the sulfur is left behind.

Pinoli
If that is raw sulfur, how are we going to convert that over to a barium sulfate precipitate?

Day
The sulfur is soluble in nitric acid. The question is whether there is any xanthate in there. Hopefully what happens is that dissolves in the nitric acid and is picked up by the barium chloride.

Pinoli
The confusing factor to me is the part of the process that if you burn off at 800°C for thirty minutes, going on the presumption that all that free sulfur has been converted to a sulfate, that it is stable.

Day
Part of the technique is to get to 800 slowly so that any non-sulfate sulfur has a chance to convert to that.

The numbers that we have always seen on sulfur have been lower than that. I don't ever remember seeing a sulfur level on a composite or on a carbon fiber above 1000 ppm, but that has always been done by the barium sulfate method by heating up the specimen slowly.

Pinoli   This concerns me with regard to current test technique and can this be extrapolated to the LECO analyzer and how accurate is that technique for measuring sulfur. Tom, are you familiar with how the LECO operates. In other words, would the LECO analyzer give you a good indication of sulfur if it is in a sulfate condition?

Paral   I am not sure how accurate it is. I would imagine you would run into some of the same problems with raw rayon. I can't give you an answer.

Pinoli   Rather than having answers, we just have more questions. I thought that as part of the issues we should ask if the current test procedure is providing accurate measurements for sodium. One of the things that we could do is have Bob run his standard test on yarn using the barium sulfate technique and transfer a samples to LECO for testing and compare the two and see if the numbers are the same. What disturbs me on that is even though the numbers may be the same, we may be looking at different forms of sulfur. I am not sure how we are going to get to that. I think that if Tom would help out and if Bob would help out, we could put a team together to go after this issue and put it to rest.

Paral   Pat, what are we going to do if we find that the numbers are right?

Pinoli	We would feel more comfortable in knowing that our test procedure is accurate at the present time for measuring these numbers and believing them. That is a very strong plus.
Paral	Will we feel the need to reduce the sulfur content?
Pinoli	I don't think so.
Day	I would say no. The spec limit is 2500 ppm and we are under that all the time. No one has demonstrated that it's a problem in performance of parts. My interest in it is the ▲ between these numbers being observed and the historical values that have always been lower. The question to me is a test method problem, not a performance problem.
Pinoli	Tony and I are going to run some fired hardware. We have already looked at char zone versus virgin material and we are going to look at ply lifted versus non-ply lifted. We want to see if there is the same concentration level of sulfur left in the char as opposed to what we went in with. Let's face it. It is still there. If you find it missing from the char zone, then it could have caused an event. If anybody wants to help out on the team, I would appreciate it.
	Bob Looney is next up on the agenda, and what I had in mind there was rayon specifications. There haven't been any changes, obviously.
Looney	Yes, there have. The ones that were shown in your presentation that you just finished. The original one was changed about 2 or 2½

years ago. We changed the denier, we changed shrinkage, we changed the pH.

Pinoli

Outside of that, nothing has changed. The other questions that I wanted to pose to North American are how are things going and is future availability a problem at this time.

Looney

Let me see if I have a flair for the dramatic. What this says, of course, is that the end of this contract will end the program for the next cou e of years at least. There will be a sufficient amount of inventory for that time. We had anticipated the possibility of this, but it was still somewhat of a surprise. We thought that there might be a couple of more years involved in the program.

Upton

When did you get this letter?

Looney

Yesterday.

Pinoli

Boy, that is timing.

Day

How long is your current contract?

Looney

It runs through September. At that time, of course, we will lose our biggest customer. We don't have the capability to down size and just run 3 machines or 2 machines to produce for the other users, which would be commercial, foreign, and military. What we are involved with now is to evaluate and think things out as to just what we can and can't do, what we are willing to do and what we are not willing to do. We will be answering to the industry,

probably to Thiokol to begin with, but you will know what your individual programs can expect. The different possibilities begin with maybe the ability to downsize to the estimated 400,000 pounds per year required for the other programs.

This does throw a monkey wrench into the plan. We had anticipated continuing as we have been. We are going to have to rethink some issues and we will just have to get back to you as far as what we are able to do.

Johnson   I want to throw 3 cents in here since I am a living expert on all the crap we went through with Avtex and before. It is very tough for the people at North American to make any kind of business judgement based on the total lack of any intelligent information coming out of DOD. I can get better information out of France that I can get out of the United States. We went through this last time with Avtex and everybody shrugged their shoulders and said they had a contract and walked away. I have already gotten one story just like that, "It's not my problem". Well, most of us have been through this and if I have one message for you, it is that you better get back to your guys who want to build these birds and tell them it is a real problem and get some reaction, or you are going to find yourself out of business. That is my prediction.

It is a terribly complex problem because they have done a marvelous job in supporting the whole program and this obviously does come as a surprise, and the thing that I know sticks in their craw at North American is that when they went into this business, some of us participated in furnishing some estimates as to what the

business was going to be and the bottom line is the business never materialized there at those levels and now we have the peace scenario and the NASA money problems. I think that if you are going to try to work together, this is a place where you need to put some real effort with your contracting system.

Hall   You know we all worked together when we had to go through it, so why can't we get the same kind of cooperation this time to keep them in business that we had to get them in business.

Johnson   There is a difference. The working together last time consisted of primarily of Col. Don Bush ramrodding all the DOD systems. NASA was always out front, but if we had not had someone with a stick to carry, or whatever you want to call it, that could talk to these various people, we would not have had nearly the information we got. We don't have a Don Bush this time. I don't even know where to go.

Mills   There is a distinct lack of coordination in the people that I have occasion to deal with. They don't seem to know what they are going to do from one month to the next. I think Wayne's point is very well taken. We need a single coordinating person, like Col. Bush was. You may or may not like everything he did, but at least he was a focal point. If this is the case, and it is going to suspend for that length of time, then we are all in trouble and NASA seems pretty short-sighted.

Johnson   There is one other element that you ought to consider in this. The letter says "effectively up to two years". I have already gone

through some numbers with Bob Looney and the fact is that my estimate, and we are the custodian of the stored yarn, is that as of the end of this contract, NASA will have in round figures 4 million pounds of rayon in stock. If you figure that a launch set takes 90,000 pounds of rayon yarn, this means that the 4 million pounds will last you 5.5 years. I am fairly guessing, and the people at Thiokol would have a lot better idea than I, that there is a year and a half's worth of product in the pipeline somewhere.

Day   It is probably not quite that high, but yes, there will be some.

Johnson   If you add that together, you have 7 years supply to drop dead use. That takes you out government fiscal year 2002. I tried to look at what would happen. The point I am coming to here is that where that letter says we may renew or want to review in two years, I would tell you that it could just as easily be 5 years. They could conveniently wait until the year 2000 and still have time to do their startups.

Pinoli   Once you go down that road of delay, it is really hard to get it reactivated. I wouldn't count on it turning on until the year just before you need it.

Johnson   That is the reason that I picked the year 2000. That is the scenario that I see.

Thomas   The other aspect of restarting, whether it is 2 or 5 years, is the startup cost and the requalification costs that could range into several million dollars. A full scale nozzle is about $5 million by

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itself. Then you have to add the startup cost to North American and the qualification costs.

Mills   Are there any other things that will be in place by 2000, environmental requirements, that a process that is not in continuous operation, be able to grandfather if you have to comply with new things? In my application, if I shut down a process, they have a whole new set of environmental requirements that will have to be met.

Looney   We are going to have the same environmental requirements regardless, but they are likely to be a whole lot stiffer at the end of this decade.

Stokes   What would be a viable alternative?

Looney   Well, you could stock pile. We could choose to stock pile and then charge for the extra costs incurred in doing that, but I don't know that we can afford it.

Mills   What would be a minimum production level that would keep you operational?

Looney   That is what we have to look at.

Johnson   Well, this is all new information. None of us knew anything about it until yesterday. I don't think any of know what the alternatives might be yet. They have only had 3-4 hours to work on the problem.

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Pinoli   Wayne, Highland is not in a position to stock pile material anyway.

Johnson   Let me be very cold hearted about this whole thing. The fact is that I don't see any reason for anybody doing anything if the services and the prime contractors won't do their end of the job. I wouldn't expect Bob to throw one pound, and I guarantee you that Highland won't throw one pound on our money.

Pinoli   I think the same will be true for ICI Fiberite. They are not going to stick their neck out.

Johnson   Why should anybody?

Pinoli   There are no guarantees out there.

Johnson   That is exactly right.

Pinoli   One last question, Bob, though maybe you won't won't to talk about this. What are we talking about in terms of cost of production? How many millions are involved?

Thomas   NASA is buying $8.9 million of rayon yarn a year.

Pinoli   Those kind of numbers are pretty small when you compare that to the overall shuttle program and you are getting some material in return. With a requal program being so astronomically expensive, you are better off just to store it with the hope that it might be used. It is really not that big of an issue. It is too small a number to have such a big impact on a program downstream.

Day	If you're looking at more than 2 years, you are looking at a full scale requalification program, which is 3 full size shuttle motors at approximately $75 million.
Hall	Sherre and I would like to say that we really enjoyed having you here and we hope that you have enjoyed your visit and if there is anything we can do for you before you leave, please ask Sherre. She will do it. We have enjoyed your being our guests and we appreciate all of you taking the time, effort and money to come here. We appreciate your company sending you here.
Pinoli	Is it over?
Hall	No, I was just afraid that we wouldn't all be together again.
Thomas	I think we owe Mississippi State a vote of thanks for their hospitality and NASA for funding a lot of these studies.
Paral	I promise that this won't take longer than maybe 2 hours. We are going to talk about SPC, but to get there we started on a TQM program and I just want to give you a couple of insights into what we have been doing. About 2½ years ago, the company president made the commitment to go after a TQM organization and implement that through the processes and through the system itself. We have done that and we have been doing it very diligently for the last 2½ years. About half way through that process, we said OK, that is not enough. We are going to take that TQM into an ISO9000 certification. By October or November of this year, we hope to have that certification.

A very key point in this whole thing is management. If you don't have management commitment all the way through, nothing will work. SPC advancements, and a strategic plan, I will get to that in just a minute.

Our senior management is committed and involved in the process. Tuesday was our quarterly TQM review. Every 3 months we go through what has happened in the plant, where are we, we are we going, and what do we need to do to get that goal, and the quality of our process. The management commitment is extremely important and it won't happen if you don't have that commitment of money, resources, equipment.

We have incorporated all of the quality elements of TQM that are best targeted to our program and I think that in most cases it is best to look at what fits your program. As you can see, customer satisfaction is number 1 on our list and that is where it belongs. The customer is who you must satisfy or you don't have a business. Continuous improvement, total involvement of all of our employees using TQM teams to encourage their involvement which is particularly important to our plant because 70% or more of our workforce is Spanish speaking. All of our supervisors are bilingual, though I am not. Other factors are performance measures of all processes and reducing costs and improving schedules.

Very quickly, we have TQM classes for all employees. The first people who had them were the management people on a Saturday, all day. Supervisors have special classes for their particular needs and just-in-time training in TQM tools and techniques.

There are 13 teams that we have already completed and there are still 3 active teams. As we find things, we implement a team. It has worked out very well.

As a comparative bit of information, you have all heard of ISO9000. ISO is really a European standards organization, but ISO really came from US MIL STD 9858. If you look at the sections that are included in ISO, they all basically came from MIL STD 9858. A lot of people don't realize that we had the tool in this country for years, we just never utilized it.

I mentioned that we are going toward the ISO certification and as I said in November of this year, we hope to have our certification completed. These steps have taken about 2 years. The biggest single effort has been documentation. It is a tremendous amount of work. There are things that we have been doing for years, but we never wrote it down, and ISO says if you don't write it down and have something that they can look at then you are not an ISO organization. That has all been done in English and Spanish.

Hill   Tom, what does it cost you to go with ISO?

Paral   Quality is not free, that is for certain. There are numerous companies throughout the US that are certified registrars and as the process begins you will send them the manuals and they are reviewed on their site and they give you lots of feedback about what you need to do. As you get farther into it, they make an on-site visit and we plan to have ours in October.

Pinoli	Tom, is it certification for the whole facility or can you break out a portion of the operation.
Paral	You can do that, although we felt that if we were going to do it, we might as well do the whole thing. However, if we had three plants, each one has to do it independently. There is a ISO9001 that is directed specifically at and R&D laboratory. The manual from ISO that tells you what you need is only half a dozen pages, but what it generates, there are things in there that cover development, laboratory process, and things like that, even for a company like ours which is primarily manufacturing.
	They give you a lot of latitude because the definitions of what you need are not spelled out exactly. You have a lot of latitude in putting together what you think is appropriate, however, you have to careful that you don't write yourself into a corner.
Bhe	Who will be doing your audit?
Paral	The company that we signed up with is in Vancouver, British Columbia, and there are several around the country that are available. It has become a business of its own.
	As part of our ISO effort, they wanted to see SPC used in the processes and we had to address that. We did not have a real good SPC personnel background to draw from and we had to hire a full time coordinator to develop the training and implementation plans. We have written our own handbook that will detail what we need at our plant and have given SPC classes for all of the employees or

will. We have given SPC charting classes to the operators and I will show you where we have started to implement some of those things out on the floor right now. We brought in a fellow from ASQC as a trainer and a speaker. He did some design of experiments, statistics for quality and engineering and process control.

This is the SPC plan for our plant. The main objectives are to identify, implement, analyze what we get, and determine a plan of action from those. I will show you some results on fabric that are encouraging. There is a lot to this. Here is the training and the major tasks. You know it has been interesting to see the level of participation by our people who have volunteered their effort.

I am not going to go through all of these, but we have identified 21 areas that we want to take a look at. These are items we felt would be appropriate to start charting and plotting. One of the first things that we did was looking at our fabric defects which is our first step in the process. What we did was start plotting visual defects and it was interesting information that we got from that. We went back with Wayne and said that we were going to do some SPC plotting and give you some information and this is an example of what we have given back to Wayne. This is a summary from April of this year. We scoured 70 rolls of material, 15,000 yards. Visually we observed about 1.5% of that as having any defect. This is not something that we would necessarily remove, but there was something in the fabric. We summarized those defects as a percentage of the yardage that we looked at.

Pinoli	Tom, when you generate your data, do you rely upon the guy who is running the equipment to input that directly into the computer?
Paral	What we did was get all the operators together and said this is a defect, this is a defect and so on, so we could have as much as a common base as we could.
Pinoli	The point is that the emphasis is on the guy who is actually doing the work.
Looney	Does he keep an attribute chart on it?
Paral	Yes he does. We have been doing this for a little over a year with Wayne and it is really an interesting exercise. I have a summary of monthly defects over that time. As you can see, we started up at 8% back at the end of 92 and within a couple of months, the response was enough to correct and bring it down to about 3.5%. We had a couple of peaks in the interim, but the last four months have relatively uniform and low. So we believe the work is paying off.
Johnson	The interesting thing about that is that this is not everything that he cuts out. It is everything he sees.
Thomas	We take each one of those monthly bullets and write up a summary sheet for each one of them, so that we know why it was low or why it was high and we identify a percent and quantity of material and this is fed back to Wayne so we can get cross communication going.

Pinoli	Wayne, when it comes back to you, what do you do with it?
Johnson	I send it to the plant. I give it to the plant manager and the qual people. For example on one of those blips there, we found out that the whole blip was made up of about 6 rolls of cloth. Since he did not have that ID on them, as soon as I saw that, I went back and identified those rolls and then we got the quality people in and asked them why they were so bad. So it provides a follow up.
Pinoli	It tells your people that there is somebody out there looking at that material. It is really a heads up.
Paral	Just to finish up, we still have things that we need to do yet, but we have broken out the elements and we are working on them and we are pretty much on schedule with our plan of implementation. I think that is about the end of my two hours.
Pinoli	I have a question. How is this feeding into ICI Fiberite?
Day	What a lead in.
Pinoli	This wasn't pre-arranged. John, why don't you come on up?
Weispfenning	I would like to talk to you a little about what we have been doing on SPC, some of the things that we have done that we think are good, things that we have learned along the way, and some of the activities that we have going on.

First, let's talk about our history. We started out in the second half of 1988 with an SPC program. It wasn't SPC then, it was SQC. Like most people, the easiest thing to do is buy a piece of equipment and start putting some data in, but we didn't. We took an existing software package that we had. We modified it a little bit so that we could get control charts and all that other good stuff. We looked at some raw material, some intermediates, like mixed resin, and finally some selected finished goods.

What I would like to do is show you some of our big successes with a product we call Karbon 647. It is used in brake discs. The constraints we have identified as a lack of knowledge.

I took this viewgraph from one of our work center managers and put this together in 91. This is our process in 1987 and this one is 1991. This is obviously a truncated data set. This is the entire data set. In this particular time in the process, any material that we generated at 10, 12, 13 or above 21, went back into the process. This is the process in 1991 and I thought that was a tremendous step. We didn't get that for nothing. That was a very major step. One of the things that I always like to point out is that SPC is not control charts. Anybody can write a control chart. If you don't understand the data, or what the control chart is telling you, it doesn't do you much good. This definition that SPC is using statistical methods for analyzing and controlling variation in a process is the one that I like.

Just as an example, each one of these is a lot of material and this is the one sigma deviation of the values that we got in the lot. We

have the ability to generate this type of curve. This is some of the same information, tests for sodium, on a more current level.

One of the things that this program makes you do is look at something a little bit differently. Along about February 1992 a number of us got together and decided that we had some good successes and we had some things that weren't so successful, and we wrote this implementation guide. We spent a lot of time looking up in the literature what actually should go into that.

What I would like to do is I would like to talk to you a little bit more about your particular product, called 4926. It is the material that we are supplying right now for the RSRM program.

The approach that we have taken is that the SPC is not an SPC program, but an MP&E program, materials, process and engineering. We want to look at the process, what we are doing with the process and how to effect improvement. This is a graph that we put together and I think that it goes up to the end of 1993. I don't think that this has any 94 data on it. If you go back in time, this is about 1992, and on this graph we have presented at % of 4926 that is shipped to specification. If you look back here, we had some pretty strange data points going on, then we implemented our MP&E process about here and you can see we are at about this level. You can't get much better than 96%.

Let's talk about why MP&E. The major problem is variability. We don't want to change the product, the composition of the product. We want to reduce the variability. This is another

interesting thing. We are probably the biggest culprit in introducing variability into our product. I think you can say that I didn't believe that when I first heard that statement. We couldn't believe that we were putting all that variability into the product. If we are doing it, then I have to believe that other people are also doing it, so maybe the 80/20 rule works here. If you are doing a process, you are probably causing 80% of the variation in that process. 20% might be caused by variability in the raw material. You have to look at that 80%, what you are doing.

Some of the conventional ways that we looked at the data weren't finding them. Our focus was to look at the manufacturing process. We teamed with our production folks, the guys who actually sit down and run the equipment. We teamed with Polycarbon to help them understand how we use their product. That teaming effort has gone on now for about 2 years. This is the mission statement that the MP&E put together.

The most important step for us to learn, the most basic thing, is the process is what the material sees, not what you think it sees, but what it actually experiences. Imagine what the yarn goes through from the time that it is made at North American Rayon. We always need to remind ourselves that the molecule is an accumulation of everything that has happened to it. Essentially, those forces that the material sees is going to define what it is.

You have to be able to do some basic things. You have to be able to measure. You have to be able to recognize patterns, and you have to be able to compare it.

In how to affect improvement, don't forget your customer. Make sure you keep him in mind. Stabilize the process where you can and follow the plan,do, study, act. We need to do things differently. We need to look at our data differently. We need to measure differently. We might need to record the information differently. Here is use the term DOE. Most of us would prefer to use the term planned experiments. Any experiment worth doing is worth planning. Make sure that you block out everything that you can.

The people at our facility have done some extremely good work at reducing variability, so much so that our governor decided to give our team the Quality Award last year.

In summation, what we find when we look at this process improvement, or TQM, or product improvement, whatever you call it, is really following the Deming cycle, the plan, do, study, act. All this space up here for planning is important. That is basically what is going on at Fiberite on SPC. It has been going on for a while and we still have a long ways to go. That is essentially all I have to talk about. Any questions?

Looney   While Keith is getting ready, I would like to share something with you. North American started implementing ISO9000 this calendar year and we also installed a new training department about this time last year and we have hired a consultant for statistical processing who is on board right now. We are doing many of the things that have been described by Fiberite and Polycarbon.

Hill   I really feel that I came with the wrong presentation, so if it switches track part way through, forgive me, but it is Bob's fault. I not going to talk about PAN unless you really want me to.

I talked to Pat a little bit about putting something together a scenario for making nozzles. If you can follow this chart, we would have someone like Eric doing characterization tests on materials that are used and then we would have those characterizations on properties that are important to the design and analysis. When this data comes in and it is fed into the design and the design is released and then we get to the manufacture. We have constituent acceptance tests which is shown here as a go/no go, prepreg acceptance, you can fix it or tweek it somehow and get it to work. Then we make a part out of that and then the part has to pass the tag end testing or it doesn't. If it doesn't, we could go through MRB and decide to use and we don't want to scrap it unless we really have to. We go ahead, use the material, and then we fire it and maybe it performs anomaly-free or it fires with an anomaly. The problem is that this presents you with a dilemma because you might not understand in terms of the characterization of the design why it performed the way that it did.

Pinoli   On your chart, I wonder how much feedback we ever get once a part is fired, as to MRB action or any decision you made during the process to gloss over things or acceptance tests that you didn't have. Does anybody record that for posterity to learn something about this whole system?

Hill   Yes.

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Pinoli   The only time you know it is if you fire it and it turns out lousy and then everybody goes around pointing fingers and saying why. If it is acceptable performance, you ignore it and walk away. MRB action, having sat on a lot of those boards and gone through that, I never saw the connect between MRB action and the end product and trying to utilize anything that came out of that. It was either accept/reject and off you go. There wasn't anybody sitting out here tabulating.

Day   Did you ever get any feedback where something went through MRB, performs and you never hear of it again? There is no learning.

Pinoli   Exactly. No learning curve.

Paral   We took a little bit different approach to that and added a level that in order for that not to be accepted before it goes to MRB, we write a non-conforming materials report that goes back to manufacturing and engineering and all the people before it even gets to the MRB. There is feedback to those groups so they can look at what happened.

Hill   One thing that really should be added here in all fairness is that besides part tag acceptance, we have SPC which is now coming on line with some of the fabricators.

Well, I am not sure how much confidence to place in this chart, but I call it an ideal scenario where the characterization tests on properties that are representative of the actual material properties of

the nozzle. I list valid design/analysis performance driven parameters where we actually do the measuring. Then design/analysis comes along and if we have the right data and the right science, the we have good design and good analysis. The models are valid because they have used all of the characterization data. Manufacturing comes along and it is all working quite well and we have constituents certified to the right properties and the process is controlled properly and the material represents what was characterized and analyzed. Then we come to acceptance testing and the acceptance test shows the material represents what was actually designed. I don't think we are there yet.

Our current acceptance testing position may be summarized by some of these points. We want something that will provide quick turn around data for accept/reject criteria so you don't hold up the line. It needs to provide some confidence to proceed with processing or to use the material. Characteristics should be short response time, inexpensive, reliable, and valid and that will give us confidence that we have what we are really after. We have heard a lot about performance based acceptance tests and we are probably going to hear a lot more about that. Sometimes something that rings a little bell is that maybe some of the proposed acceptance tests really might not fit these characteristics.

On this chart, I think that this is one of the things that SPIP has been trying to do all along, certainly with the resin work that Tom has been doing. We want to understand the as-received chemistry, and how it cures and relate that to processing parameters. Perhaps we need to develop new tests for performance based acceptance,

looking at permeability, Karl Fischer and others. We don't know how yet to handle the residual volatiles data in terms of permeability and maybe Karl Fischer would be a better way to look at that.

I think we need an increased understanding of the cured materials behavior and this might also involve understanding the basic science. 3.1 has been trying to work with this for quite a while.

Pinoli   I have pretty much given up on any guidance that we might get out of 3.1 at this point. I think that if we are going to finish this program off successfully, we should think in terms of doing it on our own.

Hill   What I have tried to do on this chart is summarize from one of our specs the extensive criteria and move ahead with that list the component tag tests from three programs here. This is the cured material tests on prepreg. As you can see, we have specific gravity, vols, flex strength, compressive strength, interlaminar double shear, thermal conductivity, and warp fill directions. When we make a part, this program has a requirement for cross-ply tensile strength, but this one does not have that as a requirement. The reason that they build this into it was because they decided that flex strength test was not telling them anything. You can see how these line up and looking at these, this is Titan right here. They kept the flex strength and they have added a vols content, a standard 4 hour test. Titan has built in an 18 hour test in addition to the 4 hour test and you can see it reflected right there in those values. This is D5 and they pretty much follow the party line, but they have a combination

of resin and vol content. They say 43% max. Well if you look up here, resin content can be 40% and vol content can be 3.5%, the most you can get is 43.5% and they have allowed you 43% max.

Pinoli   Keith, are these all manufacturers of the same prepreg?

Hill   Yes.

Pinoli   I find that number for specific gravity humorous. There is enough data out there to say that you could increase that to 1.44. You could drive a battleship through that. That is the trouble with some of these acceptance tests. They are not geared to insure a tight control of the product. They are only set as guide posts to allow you pass everything without too much difficulty.

Hill   They are all based on an acceptance philosophy of similarity to an existing database which has proven successful. I went to Titan and asked them what they use to control the resin. Do any of you recognize this? I talked to Tony on the phone and I described it so well verbally that he knew exactly what I was talking about. I asked him what you know when you see one of these and he said that if you get a scan like that you basically you know that it is a phenolic resin. I went to one of the chemists at Hercules and I showed him this viewgraph and asked him what would tell us. He said it is a phenolic. I then had enough data points to satisfy me. If you check out the peaks, qualitatively you compare peaks on this standard with peaks on the sample.

Day   Basically what you do is compare it to the last one.

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Hill   I went to Titan and said what spec controls your resin.   They
                referenced me to a MIL-R...

Day   9299. The worst spec on this planet. Have you read it? It is in a
                can and if you can pour it, it is okay.

Weispfenning   Can I say something? First of all when you attempt to describe a
                material, and when you buy a material, you might not believe that
                your specification is controlling your product. That QPL attached
                to that MIL-R-9299 is very significant. That controls the product
                that you buy. That controls their recipe and in that specification
                there is a motherhood clause and that guarantees you that it's made
                the same way. It depends on what you want in your specification.

Day   The bottom line is that there are problems with specs, but we allow
                those problems to exist. We keep on these specifications, but we
                don't go do something about it, and it is our fault for taking no
                action. We complain that some of these specs are big enough to run
                a battleship through and the reason that they are that way is
                because no one has taken action.

Mills   In cases where I have tried to take action, the customer stopped me.

Day   That is a cultural problem. It is not a technical problem. It is a
                managerial type problem.

Upton   I wonder what we are going to have at Yellow Creek.

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Mills	You might as well get out a clean sheet of paper and write your specs. If you don't, you will be locked into them. That may be a 20 year old scan using 10 year old technology, or rather technology that became obsolete 20 years ago.
Pinoli	Keith, I have one question. What is S13140F?
Hill	I will have to check it out for sure, but I believe that it is a Delta spec. It is followed by a Titan material spec.
Brown	You know I was looking at that I thought that it looked an awful lot like an Aerojet spec. We ought to just send our specs to each other and that way we could come up with data that agrees with each other and is reproducible between organizations.
Pinoli	It is hard to tell it Aerojet got it from Hercules or Hercules got it from Aerojet.
Hill	Whatever, they can have it back.
Brown	I don't know why we can't have a signoff sheet on the bottom and everybody sign off on it. We are all using the same material and that is 4926 and 5055.
Thomas	No matter what the spec is, we produce the same material.
Mills	I have 5 different specs depending on which program and I can't get those 5 Navy, Air Force and Army and whoever, to agree to change. It is a culture thing.

Day	It is the programatic nature of the business.
Mills	I still deal with people of the old school who believe that there should be a latitude there because they don't want to spend any more money. I agree with all that has been said here, but getting customers to agree to change is not easy.
Hill	Let me point out something that doesn't show up here. Do you remember that ultrasonic extraction technique. That is in everyone of our Hercules specs. The way it got there was because this committee decided that is what needed to be done. It came back up through the vendors to all of our programs. I couldn't have gone back to Hercules and sold this to the programs. It came up through the bottom. I think it was in 92 before I was even acquainted with SPIP, I was hearing talk about a new method for measuring the resin content by a different extraction and the concern was that it would give us a different database. Well, yes, but it would be more accurate, but it takes us away from our security blanket.
Mills	I have not been allowed to implement that. My customer has prohibited it on the program. He likes his old database.
Hill	I checked every spec that we have on the programs that we are now doing and found it in every one of them.
Weisphenning	The Thiokol spec has not changed.
Hall	We have to move on. We have one more presenter to get in before the tours begin.

Hill   I appreciate that. I want to show one last shot here. This is SPC data and it has to do with whether the material pocketed or not pocketed. By the way, after the announcement from Bob, I think I know of a material that will perform about like rayon in terms of char and erosion and won't pocket and there are 2 domestic sources. Everything that you had asked for 2 years ago.

Brown   What I would like to relate to you is the fair amount of data that was generated on the Peacekeeper program from 1983 to 1987. At that time the Peacekeeper program, 2nd stage, at Aerojet, some of our firings indicated that we were getting a significant amount of spallation. Spallation being synonymous with sloughing, or chunking, whatever you want to call it. What it means is that relatively significant portions of exit cone liners were being spalled out of the engine during firing operation. On dissection of those fired motors, we found that the primary source for this spallation was the low density exit cones that are associated with that motor. The standard density product that we had in out motors, we never had a problem ply-lifting or spallation, so the effort was directed toward fixing that particular problem. I believe that the plylift even that takes place precedes that and as I will show on some of the data, the event can take place very early in the firing. This shows the cross section of the exit cone. This material is the standard density product and we never had any ply-lifting or spalling with that material. This is the low density material here.

Some of you have probably seen this viewgraph before, but what I have done is I have removed some of the data that was on the original. What I have left is the low density exit cone material properties versus the motor performance. What I started out doing

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was to collect data, tag end testing data that was generated on these low density exit cones and put it all on the table to see if I could see something about where we might be having a problem.

If you start over on the left side, these are all the identifications of the motors that were fired. The F stands for Fiberite and the P is for Polymeric which is BP and moving its way into Kaiser. That tells you which material was used on what particular exit cone. There are two letters in each column. We have filler content, specific gravity of cured laminate, compression strength on laminates, compression strengths on tag ends, residual vol contents and the performance that actually occurred, whether it spalled or ply-lifted and in the last column I report the seconds that took place before the spallation event in the 60 second motor firings.

Looking at these data, one of the things that we started with was the specific gravity. We have a high of 1.03 and I can look at that data and say that I don't see much of a correlation here. We didn't see any correlation in compression strengths that we measured. They were all somewhere between 11000 and 25000 psi. One of the things that we had in our spec was the residual vol content of a tag end specimen. At Aerojet, we had a maximum requirement of 2.5% residual vol content. I might mention at this point that that particular test was considerable different from what Pat presented earlier. That particular test is done on a 1" x 1" x ¼" specimen at 225F for 2 hours. It is subjected to a desiccant drying for 24 hours prior to that period of elevated temperature exposure. That is considerably different from what Pat had indicated. Be that as it may, we show here what contents we had. We had a low of about

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0.08 and we had spalling at 0.08 and we had a high of 2.08. Here again, I didn't see anything here that told me there a correlation between residual vols and spallation. Initially I looked at some of this filler content data and though that it couldn't make that much difference. The difference seems to be around 8.4 to a high of 12.5%. The problem with that was that I was thinking of percent by weight and not percent by volume. If you take these numbers and translate percent by weight to percent by volume, these are significant difference. in microballoon content. 8% by weight in a Polymeric product translates to about 28% by volume, while a 12 or 12.5% microballoon content translates to around 45% by volume. Volume-wise you have a major change. Once I realized this effect on volume and I started looking at this, I felt that everything was falling into place. The Fiberite material in all cases was spalling and ply-lifting. The Polymeric all had no in the spallation column. There is only one case where Polymeric indicated that it did have spallation. With that in mind I summarized these items on this next chart. If you have above 10% by weight microballoons, then your cured product will consistently spall. If you have less than 10%, the you consistently do no spall.

Going back just briefly to the microballoon content versus density, you can pick out values. The solid circles are Fiberite material and the hollow circles are the Polymeric material. You can find areas where you have values of 10% microballoons giving the 1.03 specific gravity and the same 10% giving you 0.96%. There is no good correlation between the amount of microballoons that you are putting in the product and the resulting composite density.

This shows the types of microballoon contents that were associated with the materials in the motors and the type of range they are. This chart represents probably a total 10,000 of material over a period of 4-5 years. Based on this and the data that I have shown you before, is make a decision. We felt like if we had a material that was 10% or less that we would not have spallation. We went back to Fiberite and requested that they come in and produce a product with less distribution in filler content. They started supplying between 11.2 and 8.4%. When Fiberite did this, the motors that we made out of that particular product did not spallate but in some cases we did get ply lift. The Air Force's direction was to eliminate the spallation. We weren't too concerned about ply lift at the time. This viewgraph gives you a ball park score on a variety of cones and how they performed.

What I want to do here now relates to the two videos that are about 1 minute long. This doesn't really show what I wanted. What you are going to be seeing on the video is this cone is inside this one and this one is in a deployed position and what you are going to see in the film is approximately 1 minute into the firing, it will deploy. This extension cone will drop down. The first one that I have is a firing that represents a cone that had been fabricated after the request of change to Fiberite where we had them drop down to a lower filler content. I think that it is pretty representative of the change that was implemented on the program. The second video is of PQ3 and the spallation event that took place on the one Polymeric extension cone.

Pinoli   How did the post-firing analysis of that cone look?

Brown   We had cross sections of the exit cone where we had spallation taking place. From our data, what we do is when we wrap cones we keep records of the individual rolls of prepreg going into segment of the cone as you go down the line. We can go back and back track and show that where you have the heaviest spallation is where you have rolls of material that have the highest filler content.

Pinoli   Well, thanks, Gary. I guess we will now adjourn to the tours.

CINDY UPTON

SPIP

SUBTASK 3.2.1-1

ABLATIVE MATERIALS
TEST METHODOLOGY
DEVELOPMENT

Cindy Upton
May 18, 1994

Performance Based Acceptance Tests

- ## Analytical Measure of Improvement

Cindy Upton
May 18, 1994

STAGES OF TEST METHOD DEVELOPMENT

1. Preliminary Test - Test is in first stages of work.

2. Final Test - Test is ready for Round Robin testing.

3. Standardized Test - Round Robin series completed.
   Final adjustments made.
   Test is ready for implementation.

Cindy Upton
May 18, 1994

SPIP SUBTASK 3.2.1-1

CURED MATERIALS TESTING PLAN

1. Residual Stress

2. High Temperature DNS

3. High Temperature APT

4. Thermomechanical Analysis

5. High Temperature Permeability

6. Room Temperature Permeability

7. Karl Fischer Test

8. fracture Toughness

9. SRI General Support

Cindy Upton
May 18, 1994

OTHER AREAS OF INTEREST

- Carbon-Sulfur Study

- Supercritical Fluid Extraction

- Residual Vols Test

- Videotape Library

- Test Methods Manual

Cindy Upton
May 18, 1994

Planned Deliverables for FY94

- Residual Stress Test - Final Test

- APT & DNS Standardized Tests (Room Temp Only)

- Differential Scanning Calorimetry - Standardized Test

- Carbon Assay Testing - Standardized Test

- Karl Fischer Test - Standardized Test

- Permeability Testing - Room Temp. - Standardized Test
                      - High Temp. - Data gathered from PMI

- NMR - Solids Work & Final Report

- HPLC - Standardized Test

- Magneto Optical Mapping - Work with MICOM to develop

- Density Test - Standardized Test

- Chemometrics - Final Report

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REMAINDER OF CURRENT SPIP

PRIORITY

1. Performance Based Acceptance Tests

2. Plylift TQM Team (3.1)

3. Large Scale SRCS

4. UVF Technique (Bondlines)

5. Materials Database (3.1)

6. Structural Code (3.1)

7. In-Process Cure Monitor (Bondlines)

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May 18, 1994

NASA RESEARCH ANNOUNCEMENT

NRA 8-10

- Industry Briefing/NRA Release - April 20

- Proposals Due - May 20 & July 20

- Evaluations Completed - June 20 & August 20

- Contracts Awarded - Oct. - Dec.

- This NRA gives Industry a chance to tell NASA what needs to be done to improve the reliability and performance of solid rocket motors

Cindy Upton
May 18, 1994

Criteria for Evaluating NRA

- Technical merit of proposal. What is the National Outcome of the work?

- What does the company plan to contribute? (i.e. manpower, facilities, etc.)

- How will the work be implemented into Industry?

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May 18, 1994

Currently, SPIP is planned to end in FY97. If SPIP is extended, Industry will probably be asked to contribute a great deal of cost sharing.

Cindy Upton
May 18, 1994

MAGNETO-OPTICAL MAPPER

Charles R. Christensen, Joseph K. McDonald, Frederick W. Clarke, John A. Grisham, and Theodore C. Leslie

Weapon Sciences Directorate
R, D, and E Center
MICOM

and

George A. Tanton
Teledyne Brown Engineering

MICOM MOR: TECHNICAL ADVANTAGES

MOR WIDELY APPLICABLE
applicable to both high and low symmetry molecules

ADDITIONAL SPATIAL AND ANALYTICAL INFORMATION OBTAINABLE FROM MOR MAPPING
information on degenerate states possible
improved spectral resolution possible

INCREASED SENSITIVITY OF MOR DUE TO IMPROVED TECHNOLOGY NOW AVAILABLE
resulted in reviving interest in mor
mor less sensitive to scattering than absorption methods
rotation determined directly

Polarizer

magnetic field

Constant
magnetic field

Polarizer
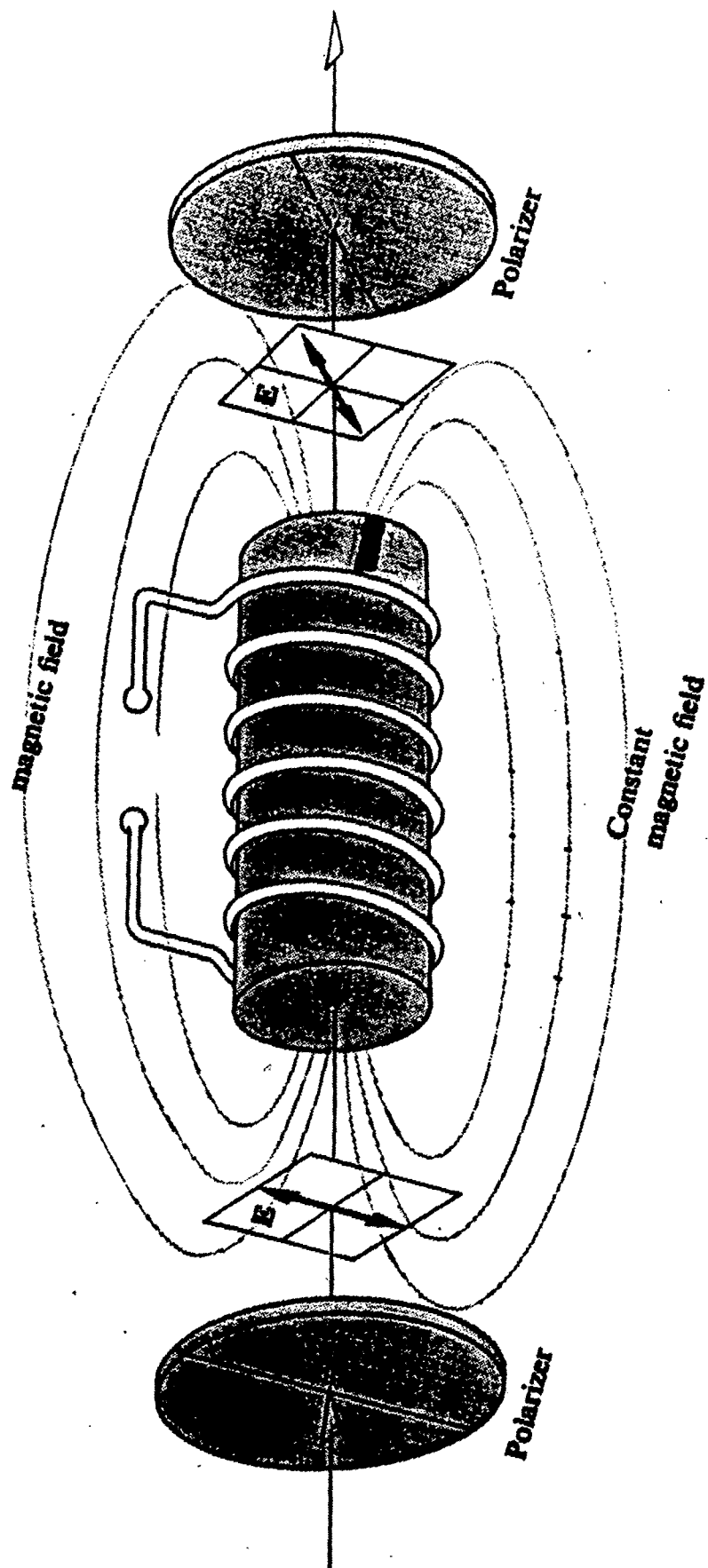
FARADAY ROTATION

FARADAY ROTATION
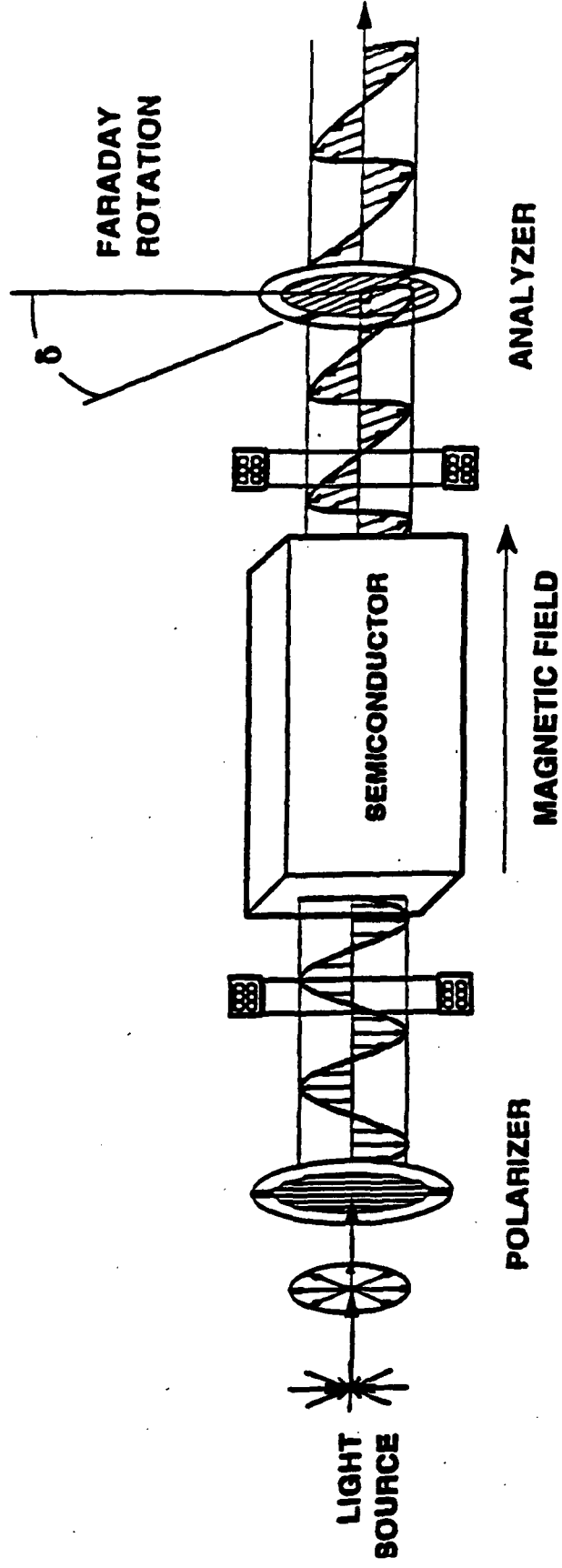
CHEMICAL AND MATERIAL SCIENCES
FT-IR-MOM

Objectives:

o   Show that FT Spectrometer can be used as light
    source for MOR

o   Characterize semiconductor materials to
    compare with previous results

o   Extend Faraday rotation research to new
    materials

FT-IR

POLARIZER

SAMPLE

MAGNET

ANALYZER

MCT DETECTOR

Eperimental Set-up
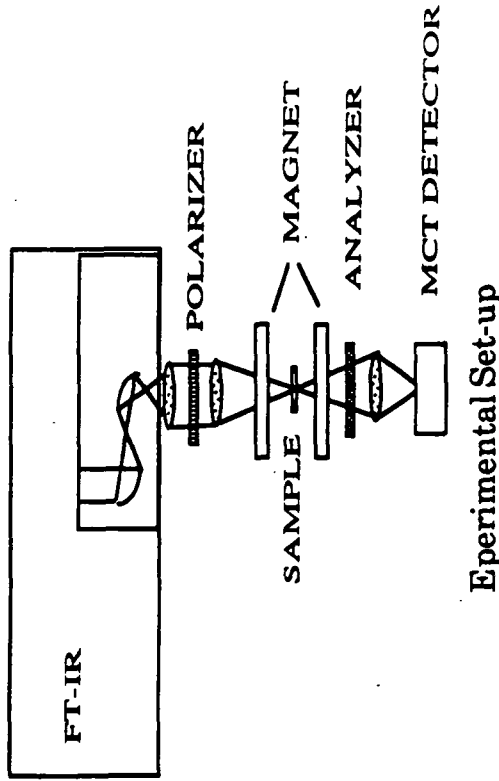
MOR Spectrum of HgCdTe

HgCdTe Transmission Spectra

MANUFACTURING

Polymers Composite Failure Analysis
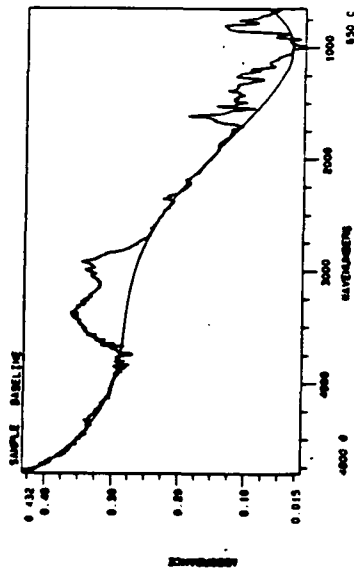
Spectra of uncured composite mat;
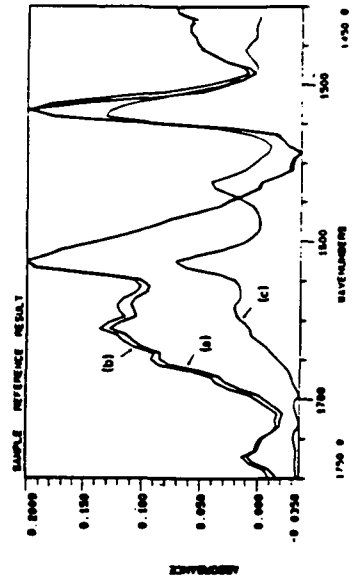
Overlay plots of the spectra of the composite mat and extracted resin; (a) sample, cured; (b) reference, uncured; (c) result, resin.

RESIN
CARBON FIBERS
POLYESTER FIBER MATRIX
RESIN

Schematic representation of composite mat.

FUTURE PLANS

COMPOSITE STRUCTURES
STRUCTURES DIRECTORATE - Donald J. Jaklitsch
NASA, Materials and Processes Laboratory - R. C. Clinton

MEDICAL APPLICATIONS

ENVIRONMENTAL

SEMICONDUCTOR MANUFACTURING

CUSTOMER SUPPORT
    JAVELIN
    BMDO
    OTHER GOV. LABS.

TI MAPPER
    IN HOUSE
    SUPPORT JAVELIN OR BMDO AT CONTRACTOR

MAGNETO-OPTICS: DUAL USE APPLICATIONS
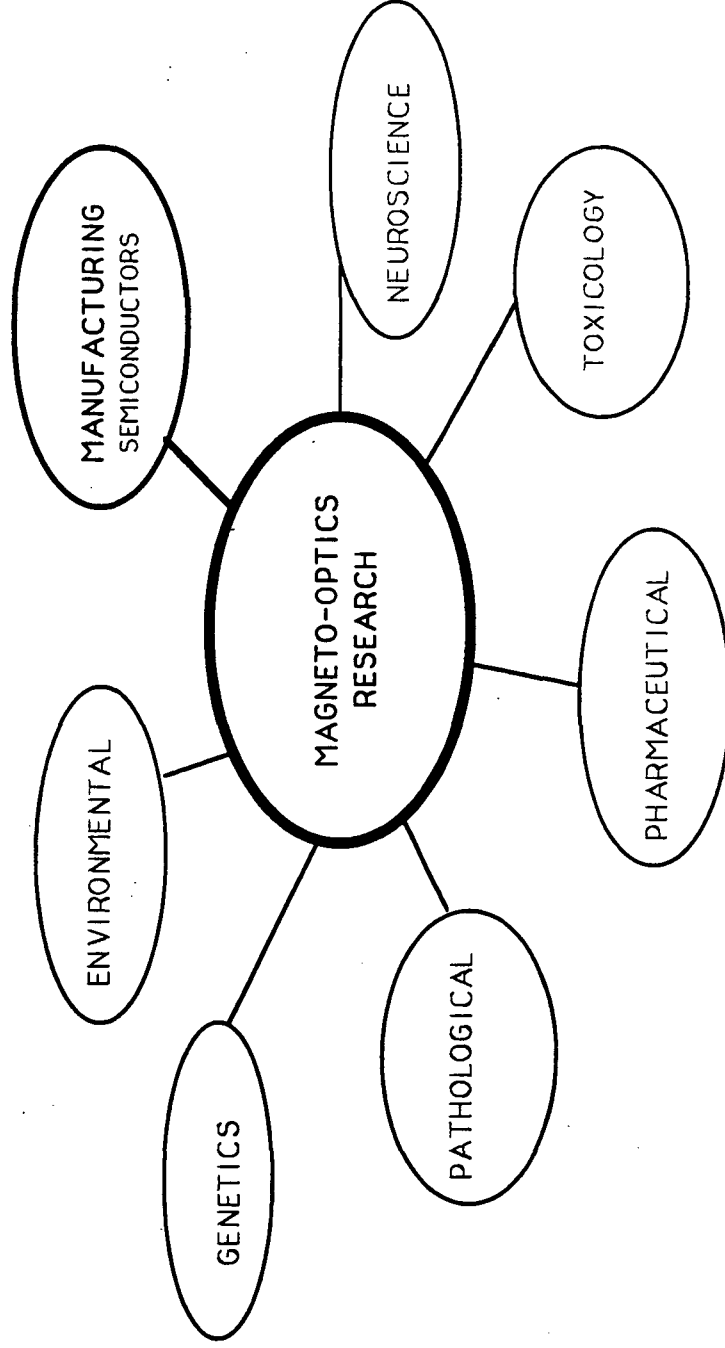
FRANCES ABRAMS

COMPUTER AIDED PROCESSING OF COMPOSITES

by Frances Abrams
Wright Laboratory
Materials Directorate
Wright-Patterson AFB OH

MAY 17, 1994

FOR THE
SPIP - NOZZLE INITIATIVE ADVISORY COMMITTEE ON
CARBON PHENOLIC CONSTITUENT
AND COMPOSITE TEST METHODOLOGY

Intelligent Materials Processing

The *efficient* transformation of a material into the *required condition* with *required properties*.

- Efficient (rapid, affordable)
- Required condition (shape, microstructure)
- Required properties (mechanical, thermal, electrical, ablative)

Efficient Processing

- Lower the Intercepts
- Integrated Process & Design
- Low Capitol Expenses
- Inexpensive Materials
- Increase the Slopes
- Intelligent Processing
- TQM

Development

Production

Cost per Part

Number of Parts
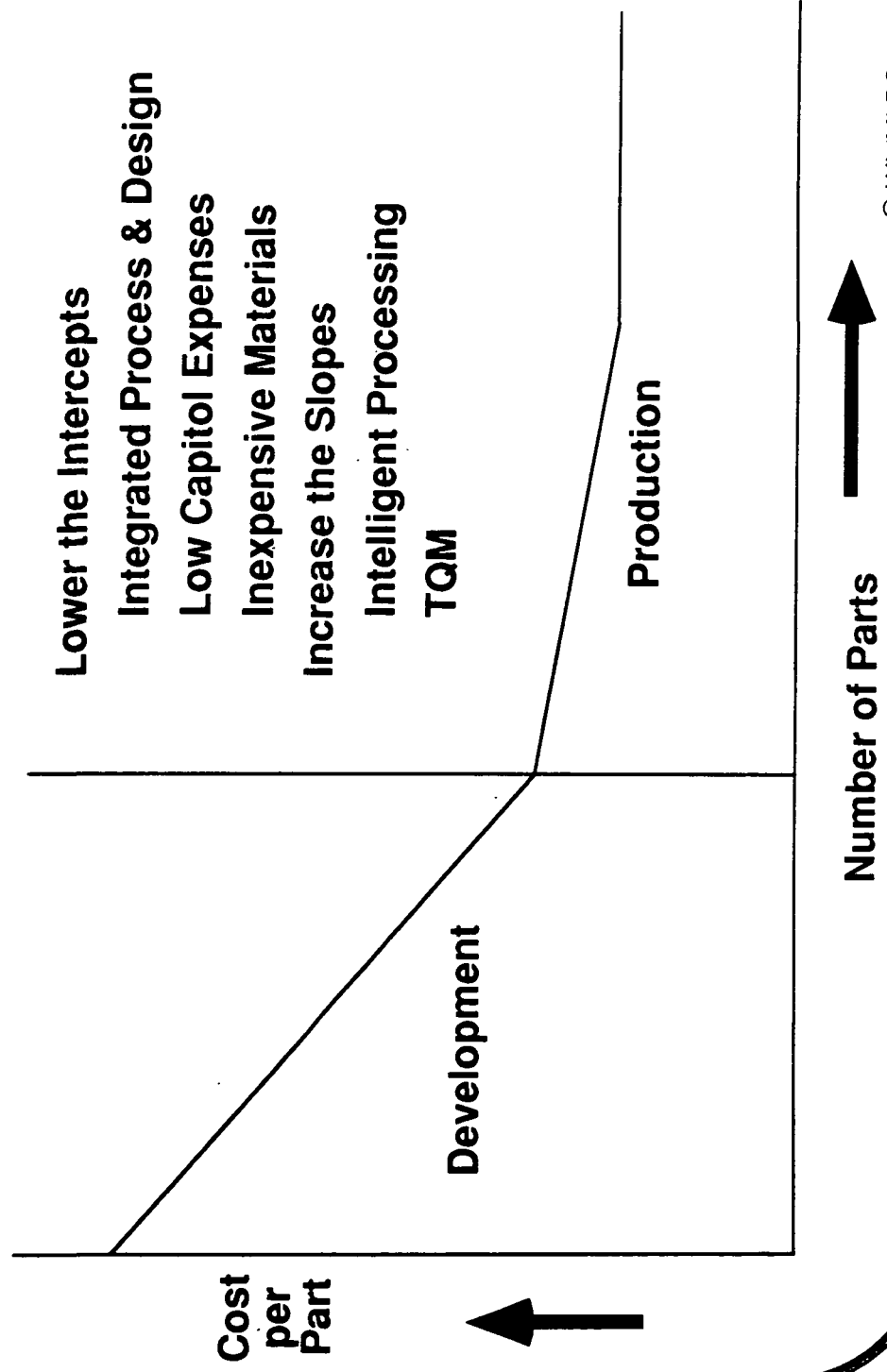
Production Number Strongly Affects
Cost Drivers

250 Production
AV-8B Aircraft

Recurring Costs
93%

5.3% Tool Design
and Fabrication
1.7% Other Nonrecurring

2 YF-23 Prototype
Aircraft

Recurring
Costs
6%

28% Tool Design
and Fabrication

84% Other Nonrecurring

GP24-0136-1-DAch
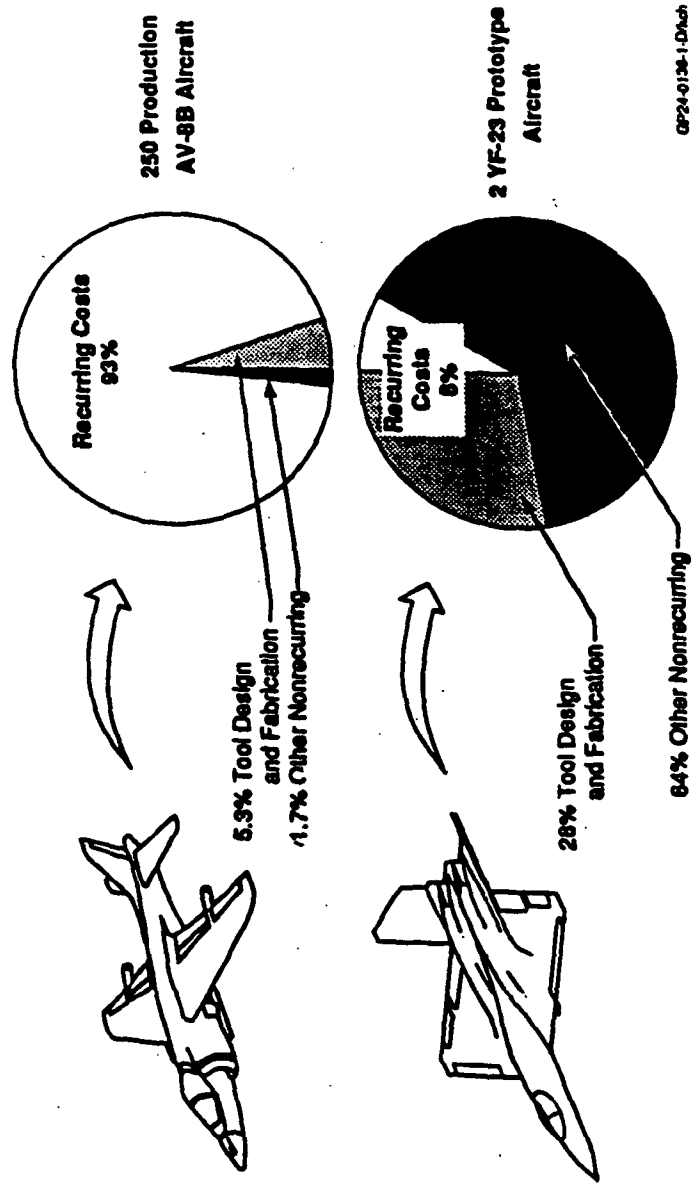
Figure 3.1–2. Composite Structural Costs
Reduced Quantity Leads to Significant Impact of Tooling and Nonrecurring Costs

Goal Oriented Processing
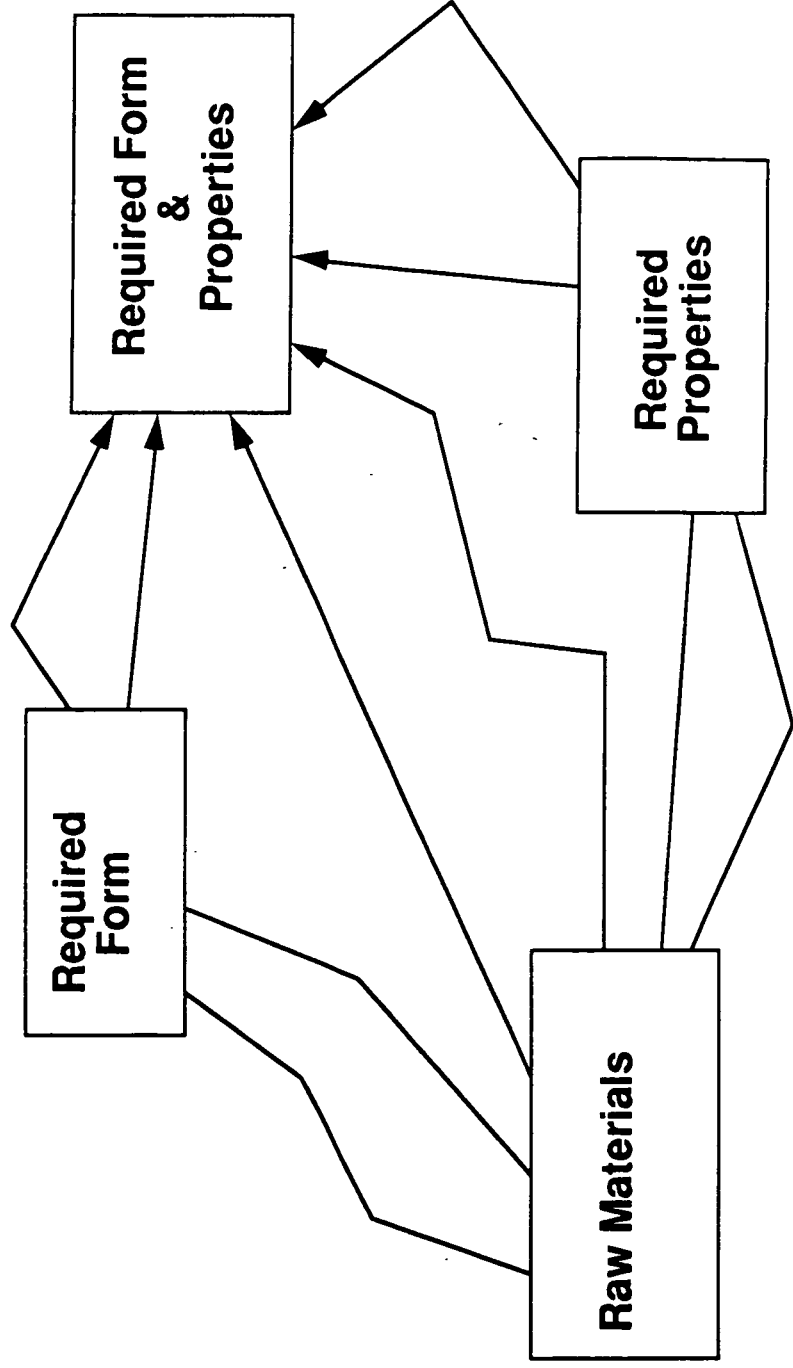
Tools for Smart Processing

Process
Experiments

Neural
Networks

Data Bases

Models

Engineering
Judgement

Expert
Systems

SPC

DOE

Sensors

© WL/MLBC 5/11/94
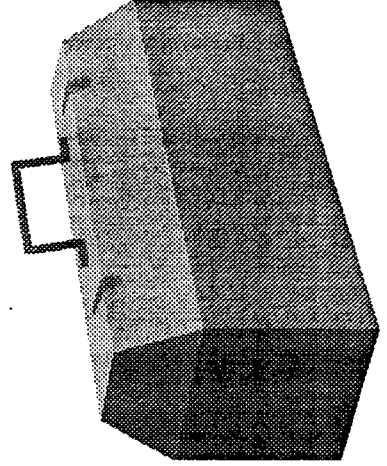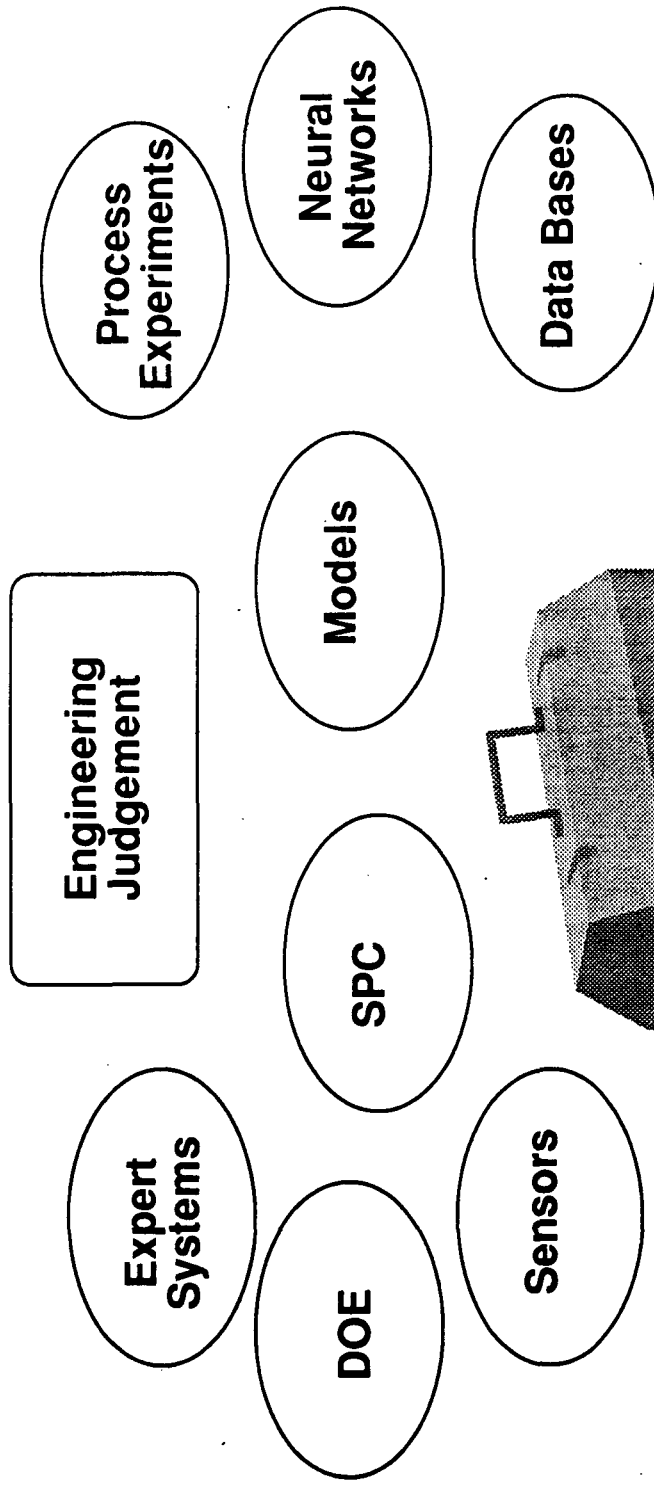
Trial and Error Development

Process Experiments

Design of Experiments

Input → [Black Box] → Output
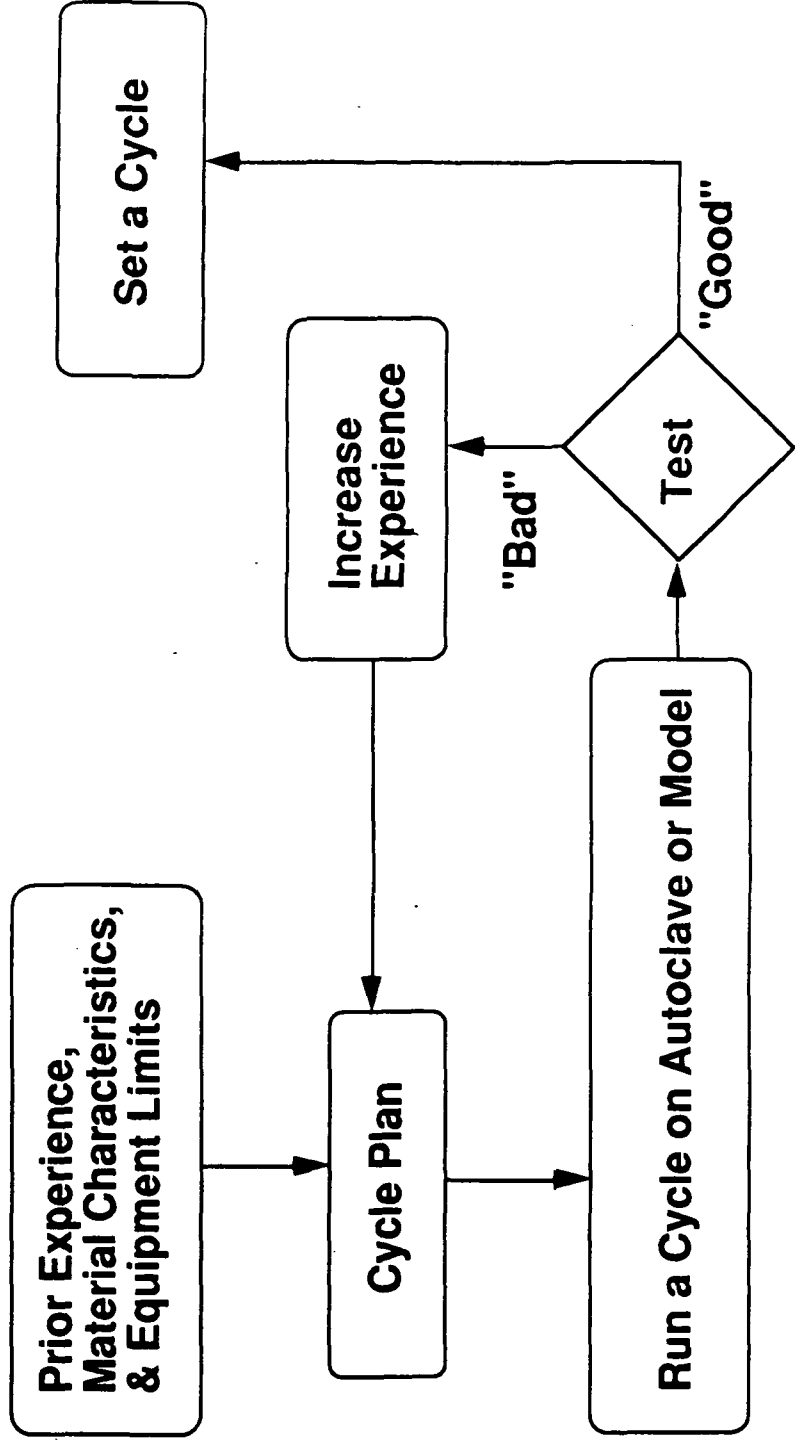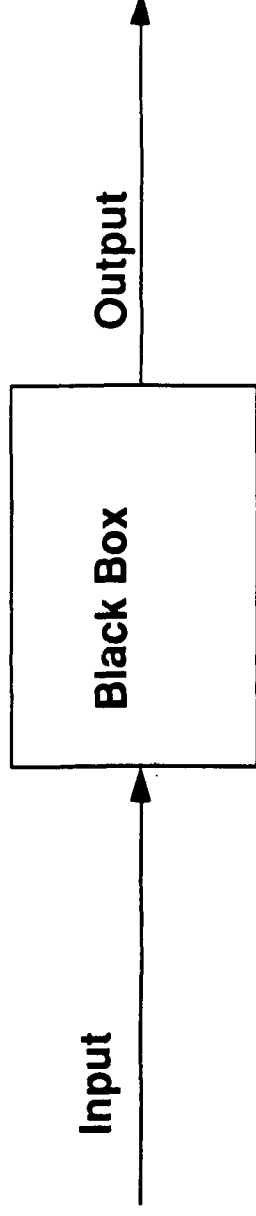
Uses

Process Control for Large Production Lots

Continuous Process

Limitations

Batch Processes (Infinite Variation)

Small Lot, Expensive Products

Multiple Interactions Between Variables

Bagging Variables

Separator Materials

Teflon film with Holes on 1/2" Centers

Phenolic Laminate

Tooling Plate

GAP

Caul Plate

Nylon Bagging Material

Breather

Breather

Breather

Nylon Bagging Material

Breather Material and Location

Non-porous Release Film

Damming Material

Process Experiments
Design of Experiments

Temp

How Many Possible Pathways?
How Many Can We Afford to Try?

Time

Statistical Process Control

Run Process → Monitor Process Variations → Track Product Quality → Statistically Evaluate Effects → Change

Change — Yes → Correct Process

Change — No

Correct Process → Run Process

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Statistical Process Control

Uses

Maintaining Consistancy
Recognizing Problems
Improving Process Controls

Limitations

Requires Some Failures
Small Numbers May not Be Statistically Significant
Black Box Model Assumed
Statistics Can be Misleading
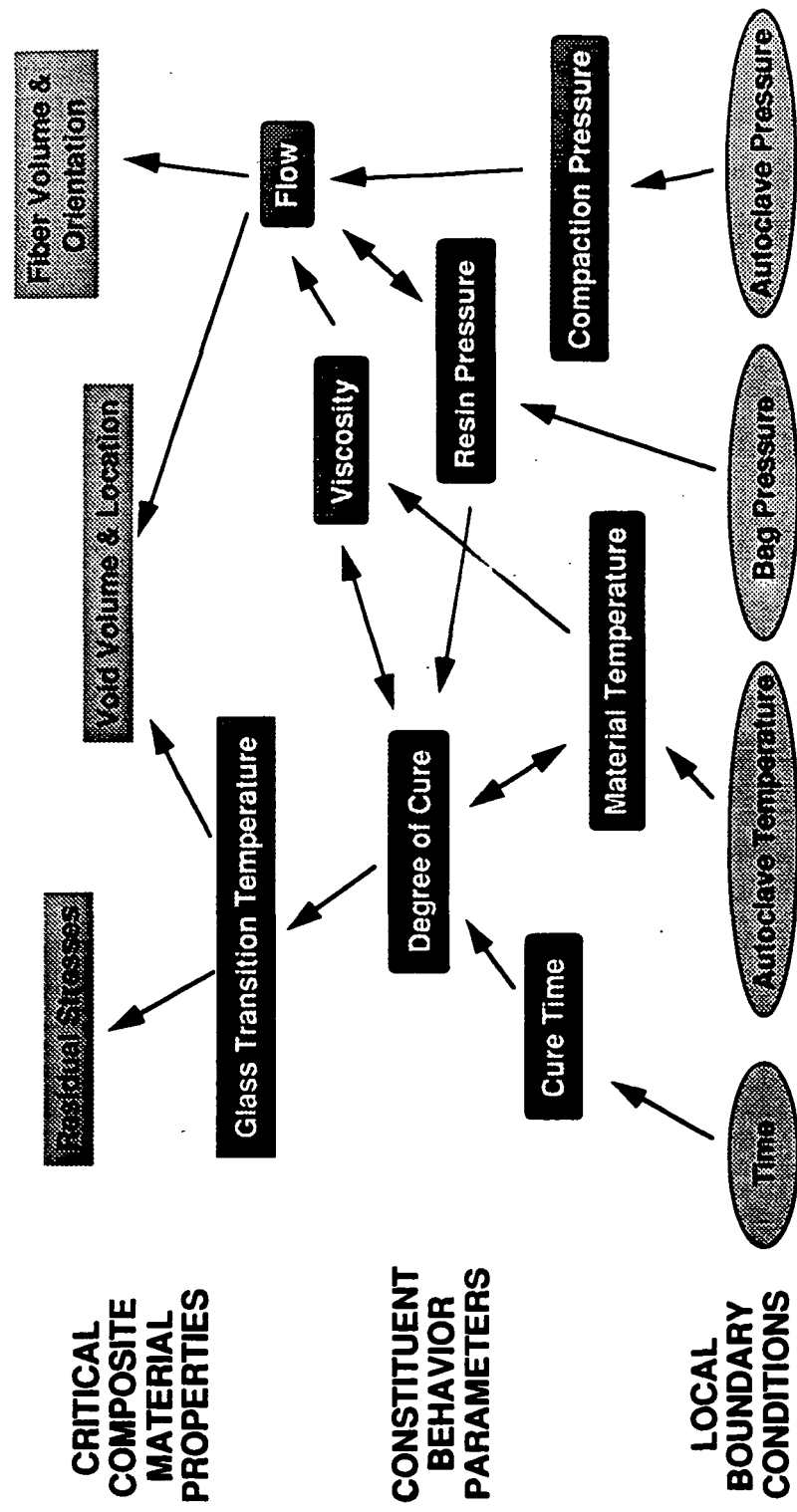
Influence Diagram of Autoclave Curing of Polymer Composites

CRITICAL
COMPOSITE
MATERIAL
PROPERTIES

CONSTITUENT
BEHAVIOR
PARAMETERS

LOCAL
BOUNDARY
CONDITIONS

Fiber Volume & Orientation

Flow

Void Volume & Location

Residual Stresses

Glass Transition Temperature

Viscosity

Resin Pressure

Degree of Cure

Material Temperature

Cure Time

Compaction Pressure

Autoclave Pressure

Bag Pressure

Autoclave Temperature

Time

Comparative Thermal Analysis
SC1008/T40 Carbon-Phenolic

RDS
(G' & G")

DSC
(mCal/sec)

TGA
%Wt. Loss)
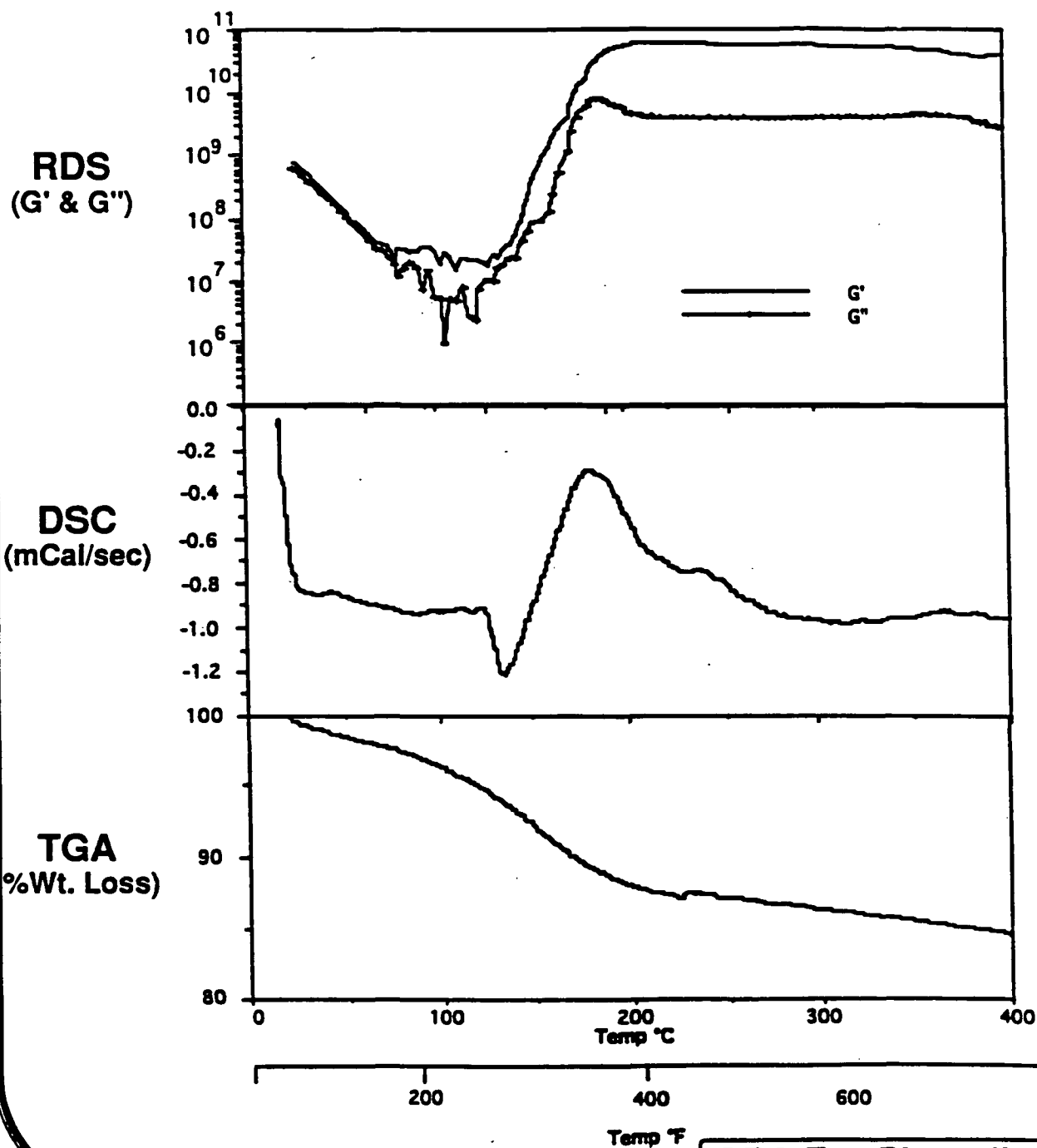
QPA For Phenolics

Computer-Aided Cure System

Concept World
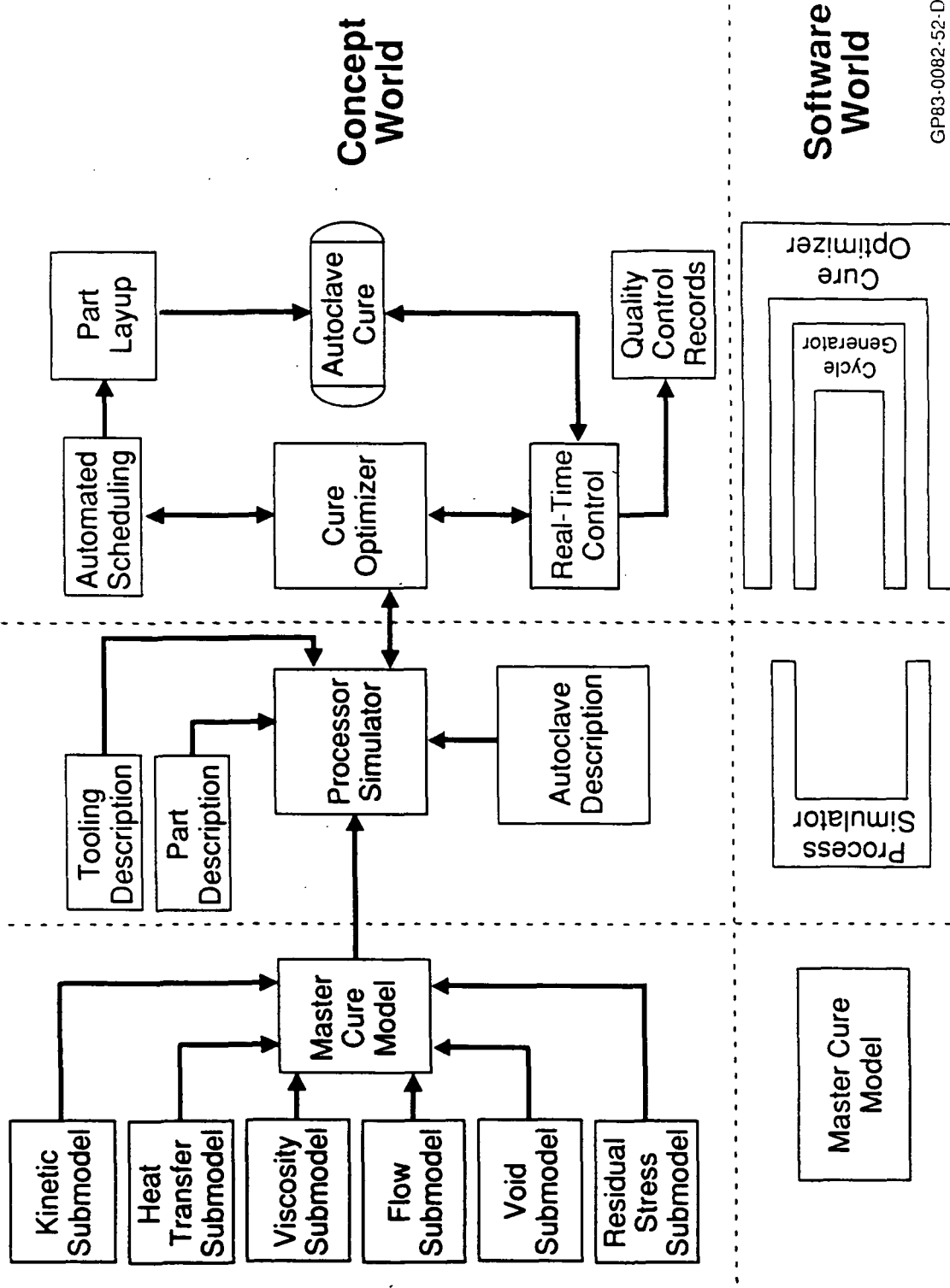
Software World

GP83-0082-52-D

Master Cure Model Data Base

Non Porous Materials

Cp, K, ρ

$Cp, K, \rho, dia.$

$E_1, E_2, G_{12}, G_{13}, G_{23}, \nu, \alpha_1, \alpha_2$

Bag

Breather

Caul Plate

Bleeder

Peel Ply

Prepreg

Resin | Fiber

Tool

Part Data
- Geometric Shape
- Ply Directions
- Mode Control

Porous Materials

$Cp, K, \rho, A, B, C, D, E$

$A, B, C, D, E, Resin Content$

Cp, K, ρ
$\dfrac{d\alpha}{dt} = f(\alpha, t)$
$\eta = f(\alpha, t)$

GP93-0082-16-D
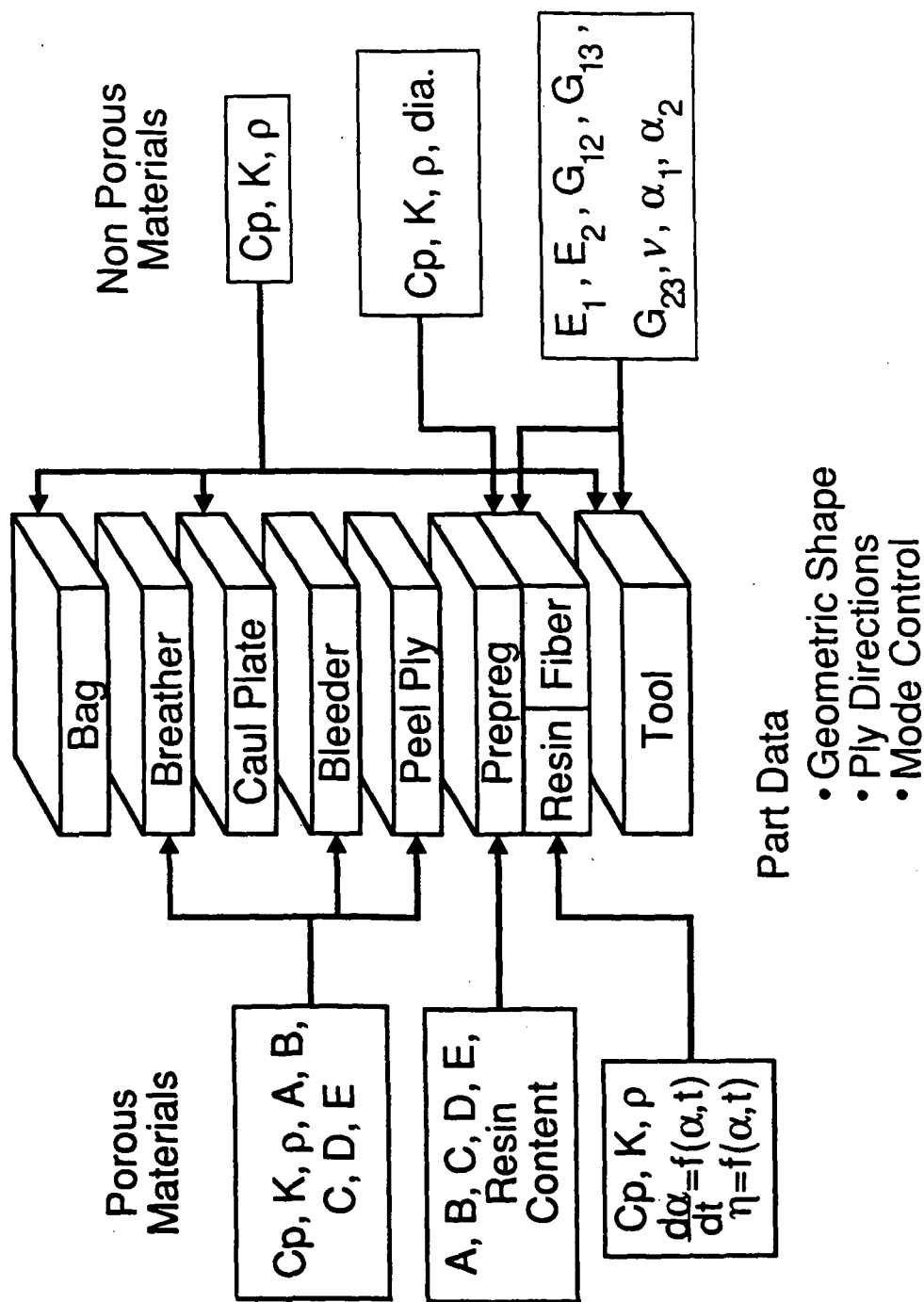
Process Models

Uses

Parametric Studies to Develop Expertise

Study Interactions

Virtual Sensors

Limitations

Often Expensive to Develop

Require Extensive Data

Models are not Reality

Expert System Off-Line

Expert System

Cycle Plan → Model Cycle or Part Cycle → Test

"Bad"

"Good" → Set a Cycle
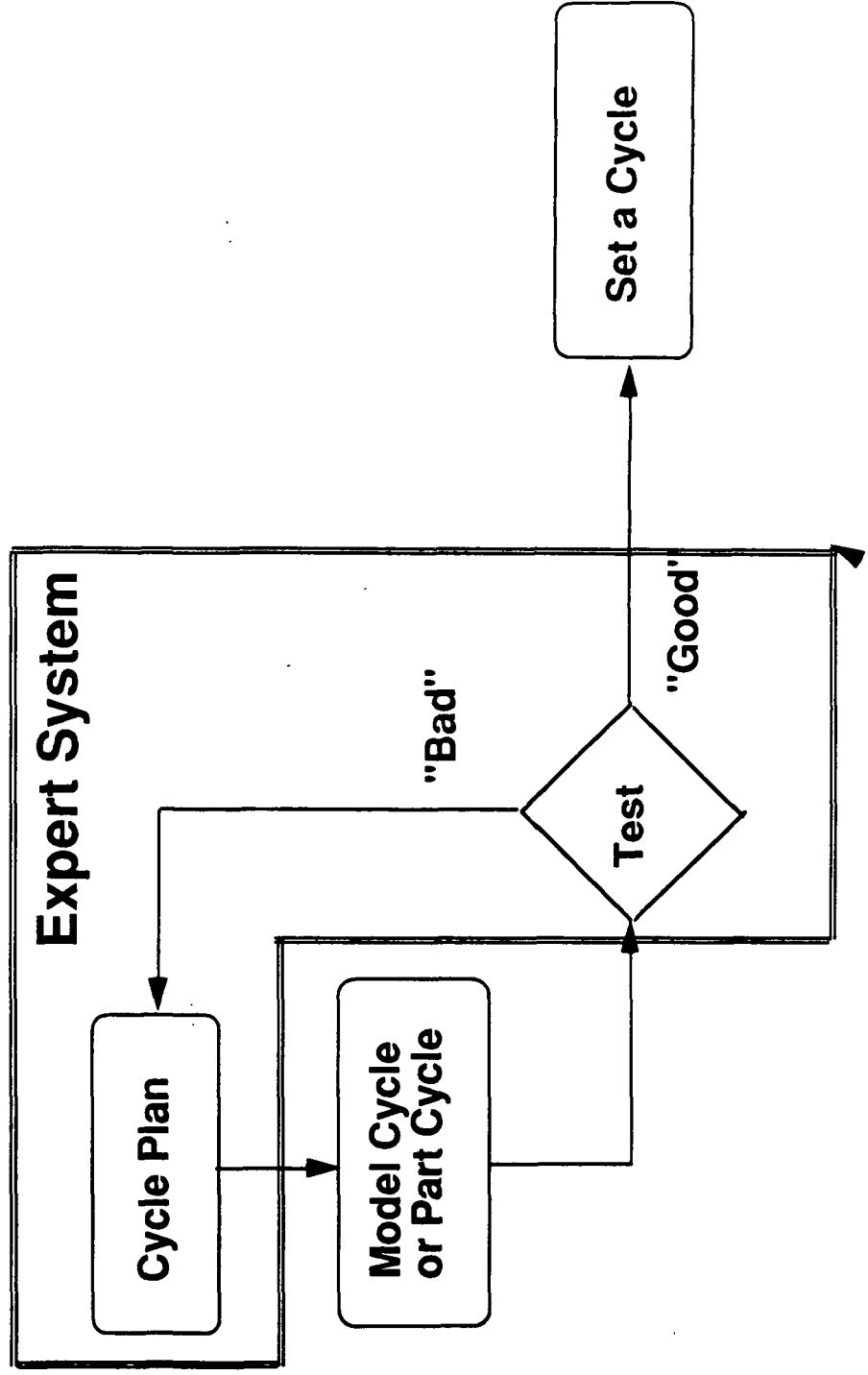
Sine Wave Spar Cure Cycle

Standard (min)	Optimize (min)	Reduction (min)	% Time Savings
840	540	300	36

GP93-0082-6-D
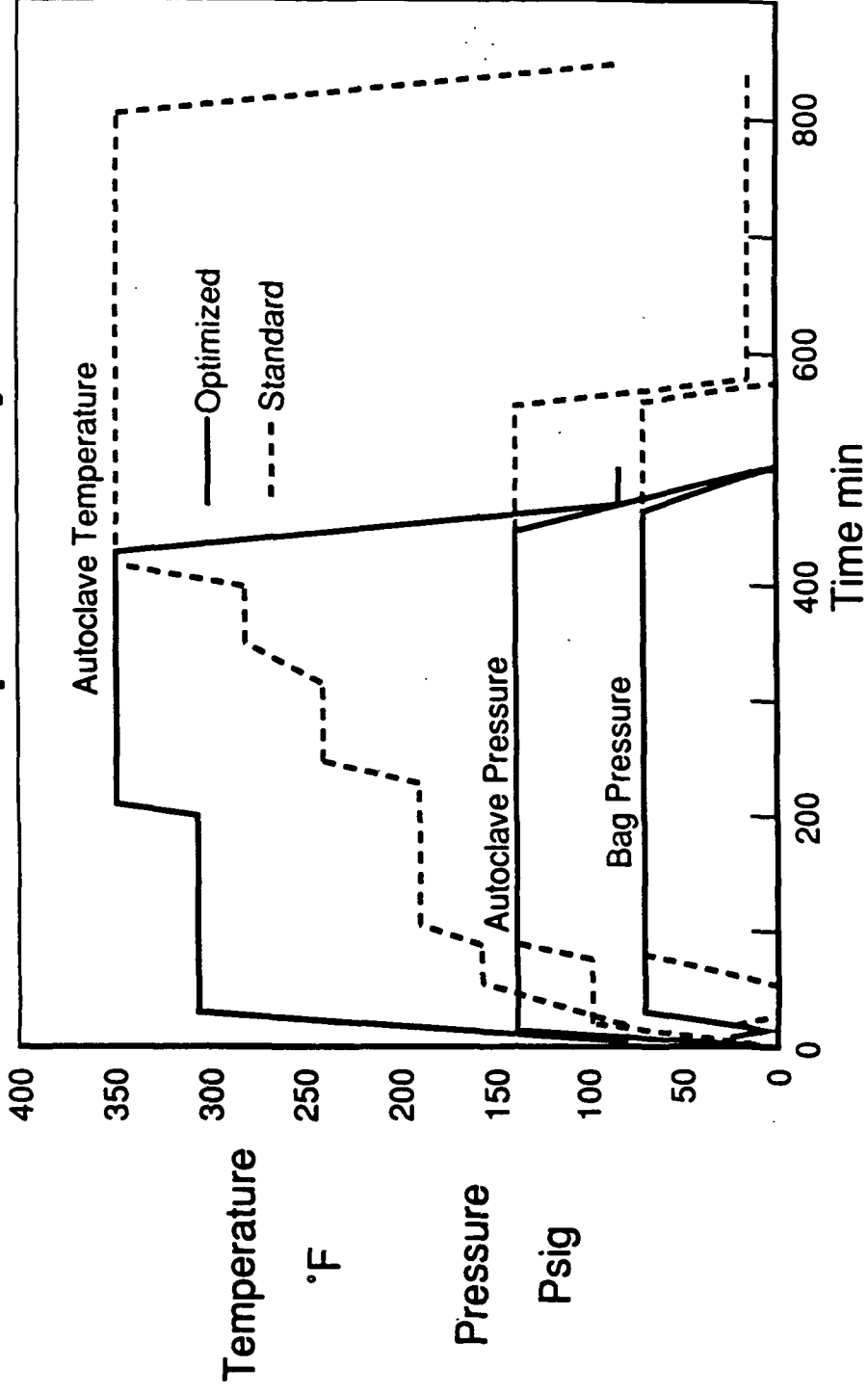
In-Process Measurements

Boundary Conditions

Temperatures

Pressures

Laminate Conditions

Dielectric Properties

Pressures/Stresses

IR, UV, Visual Spectroscopy

Void Formation

Patterns

Heat Flow

Resin Flow

Vitrification/Gelation

Thickness Change

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Dielectric & Rheology

Legend:
- LOGE2 (arb.)
- T1 (F)
- LOGG" (arb.)
- T2 (F)

x-axis: time (min) — 0, 50, 100, 150, 200, 250, 300

y-axis: 0, 100, 200, 300, 400, 500

GRANULARITY

SENSED VALUE (vertical axis)

TIME
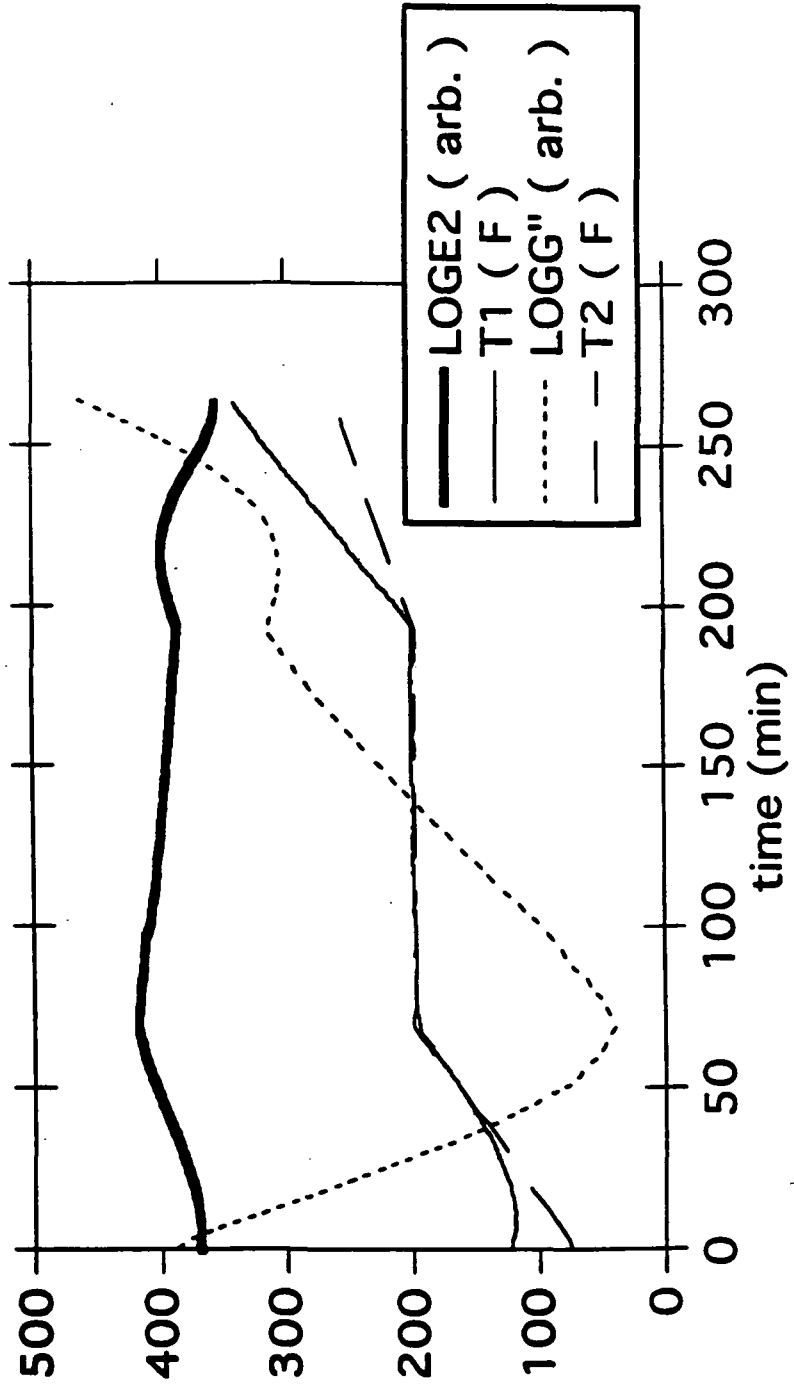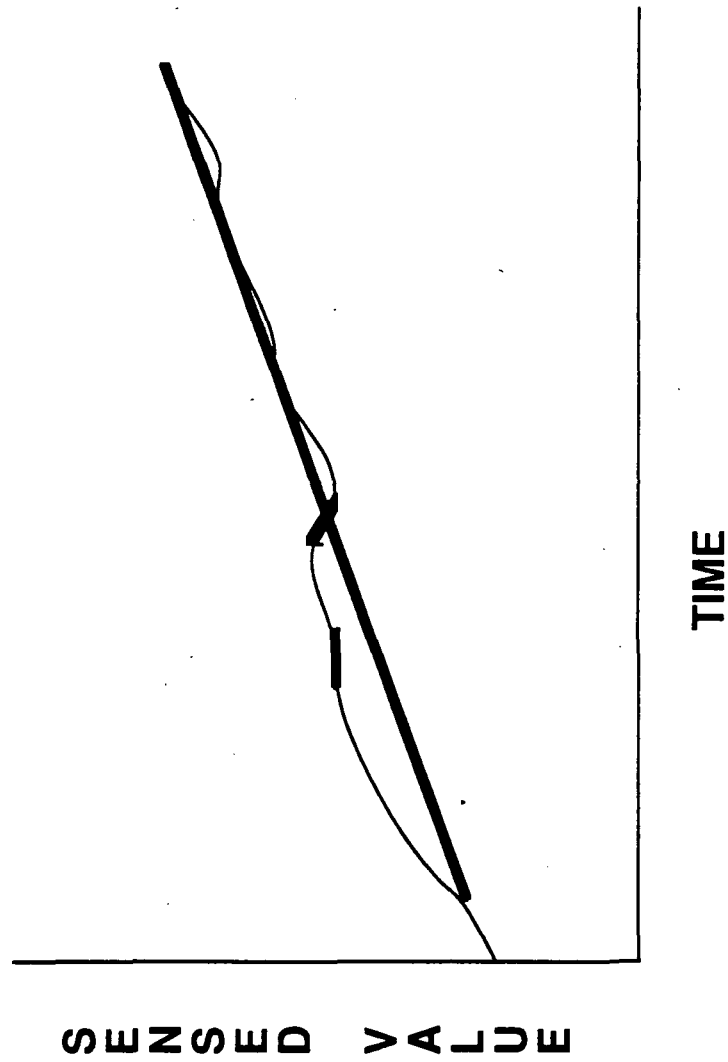
WHICH REPRESENTS THE SLOPE OR RATE OF CHANGE?

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In-Process Measurements

Uses

Model Development & Validation

In-Process Control

Quality Verification

Limitations

Generally Local

Often Indirect

Confusing Influences

Inconvenient

In-Situ Expert System

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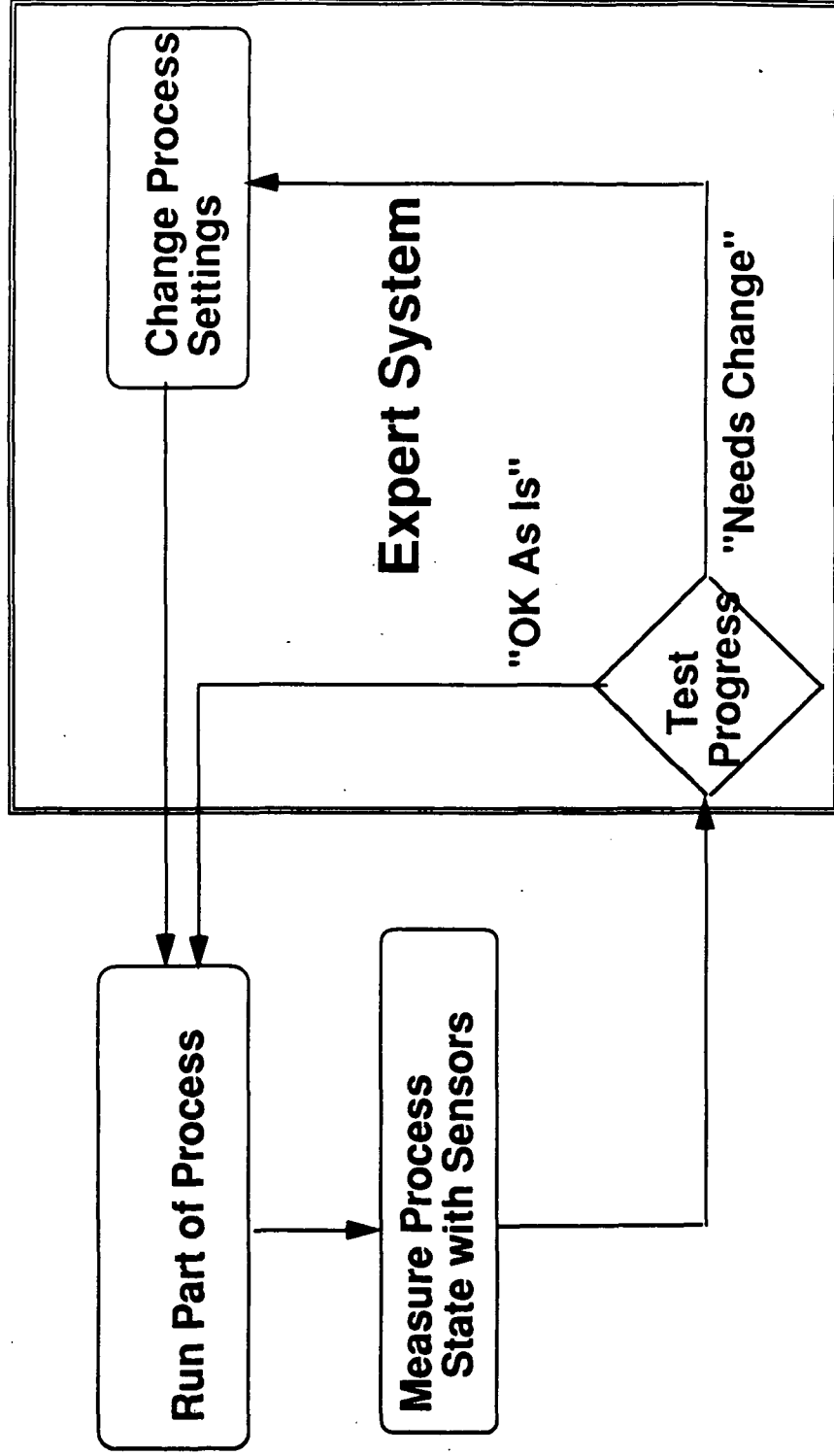
Processing Specifications

Process 1

Apply 28 ± 2 inches vacuum.

Apply 85 ± 10 psig pressure.

Heat at 2-5 F to 180 F

Hold for 60 ± 10 minutes at 180 F

Vent vacuum

Heat at 2-5 F to 350 F

Hold at 350 F for 120 ± 20 minutes

Cool at 2-5 F to 150 F

Release Pressure

Process 2

Drive north at 55 mph for 15 ± 2 min

Turn right

Drive 55 mph for 2 ± .5 min

Turn left

Drive 55 mph for 2 ± .5 min

Turn right

Drive 55 mph for .5 min

Turn left

Drive 55 mph for .5 min

Turn right

Drive at 25 mph for .3 min

Turn right

Drive at 15 mph for .5 min

Process Strategies

Process 1

Apply full vacuum (no leaks)

Heat resin as fast as possible without getting large temperature gradients until viscosity drops

After viscosity reaches minimum, apply enough pressure to prevent water vapor and release vacuum

Heat until desired glass transition temperature is reached

Hold until cure is complete at this temperature

Cool until maximum temperature is below boiling point of water

Process 2

Travel north on St. Rt. 4 to US 40 (third light after crossing I-70)

Turn right on 40 to St. Rt 571 (1st light)

Left on St Rt 571 to Milton-Carlisle (1st stop sign)

Right on M-C Pike to Funderberg (!st left)

Left on Funderberg Rd to Sheryl (1st right)

Right on Sheryl to Teresa (1st right)

Right on Teresa to end of lane (Red house with brown trim)

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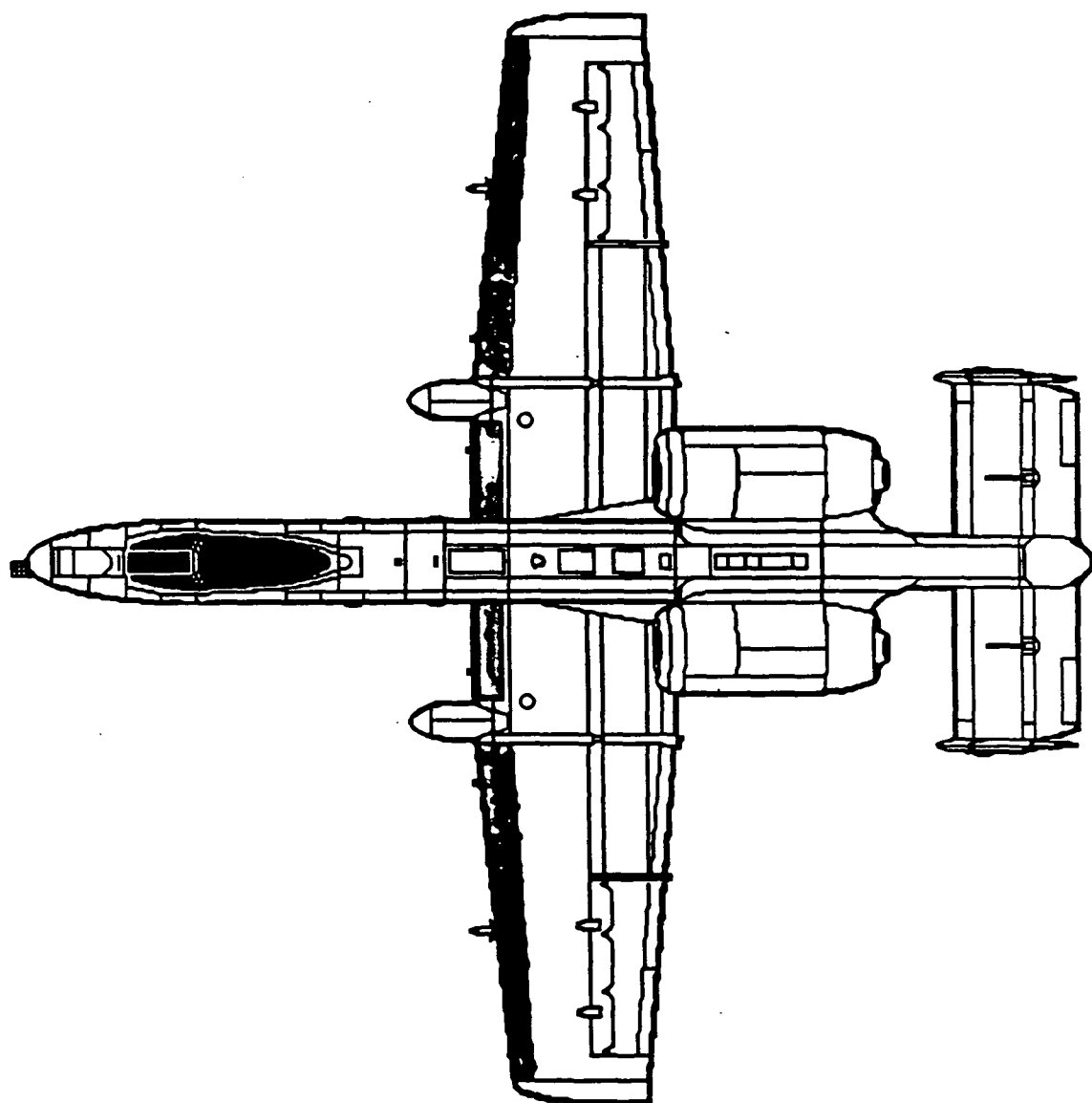
Air Force Implementation

Sacramento Air Logistic Center (1990)
Projected A-10 Leading Edge Production Savings = $4,000,000+

DoD Industry (A/C Composite Parts)
Projected Production Savings = $5M/year

Production Autoclave Cure Cycles Shortened by 70%

Mechanical Properties		QPA	Conventional
0 Tension	Strength	273 ksi	260 ksi
	Modulus	21 Msi	21 Msi
90 Tension	Strength	8.2 ksi	7.5 ksi
	Modulus	1.6 Msi	1.4 Msi
0 Tension	Strength	251 ksi	245 ksi
	Modulus	20.9 Msi	21 Msi
90 Tension	Strength	5.25 ksi	5.27 ksi
	Modulus	1.3 Msi	1.31 Msi
0 Compression		228 ksi	231 ksi
Iosepescu Shear		15.5 ksi	14.7 Msi

Late Pressure Application (100 psig)

Legend:
- LOGE2 (arb.)
- T (F)
- P (psi)
- -5*PHI (deg)

x-axis: time (min), 0 to 250

OPA For Phenolics

Early Pressure Application (100 psig)

Legend:
- LOGE2 (arb.)
- TEMP
- P (psi)
- -5*PHI (deg)

x-axis: time (min), 0 to 400

y-axis: 0 to 500

Early Pressure Application (175 psig)

Legend:
- LOGE2 (arb.)
- T (F)
- P (psi)
- -5*PHI (deg)

time (min)
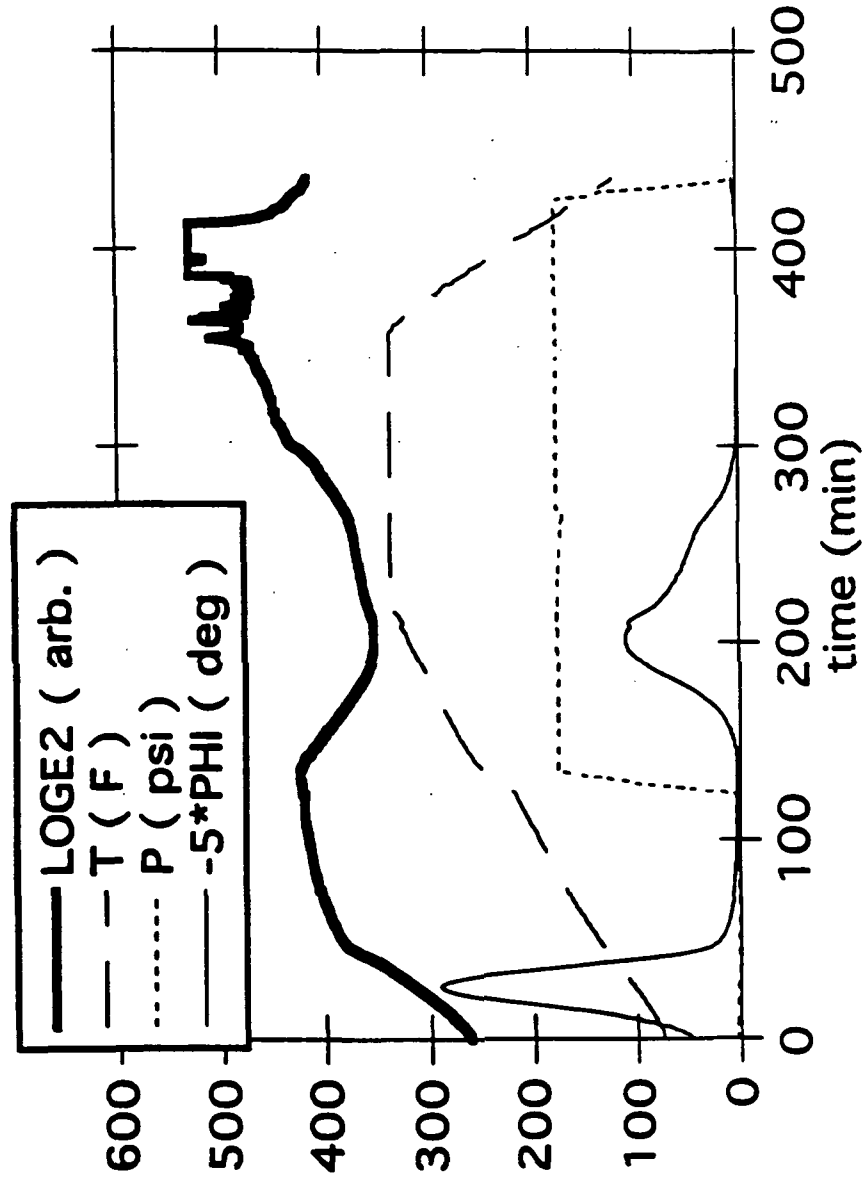
A Cure Strategy
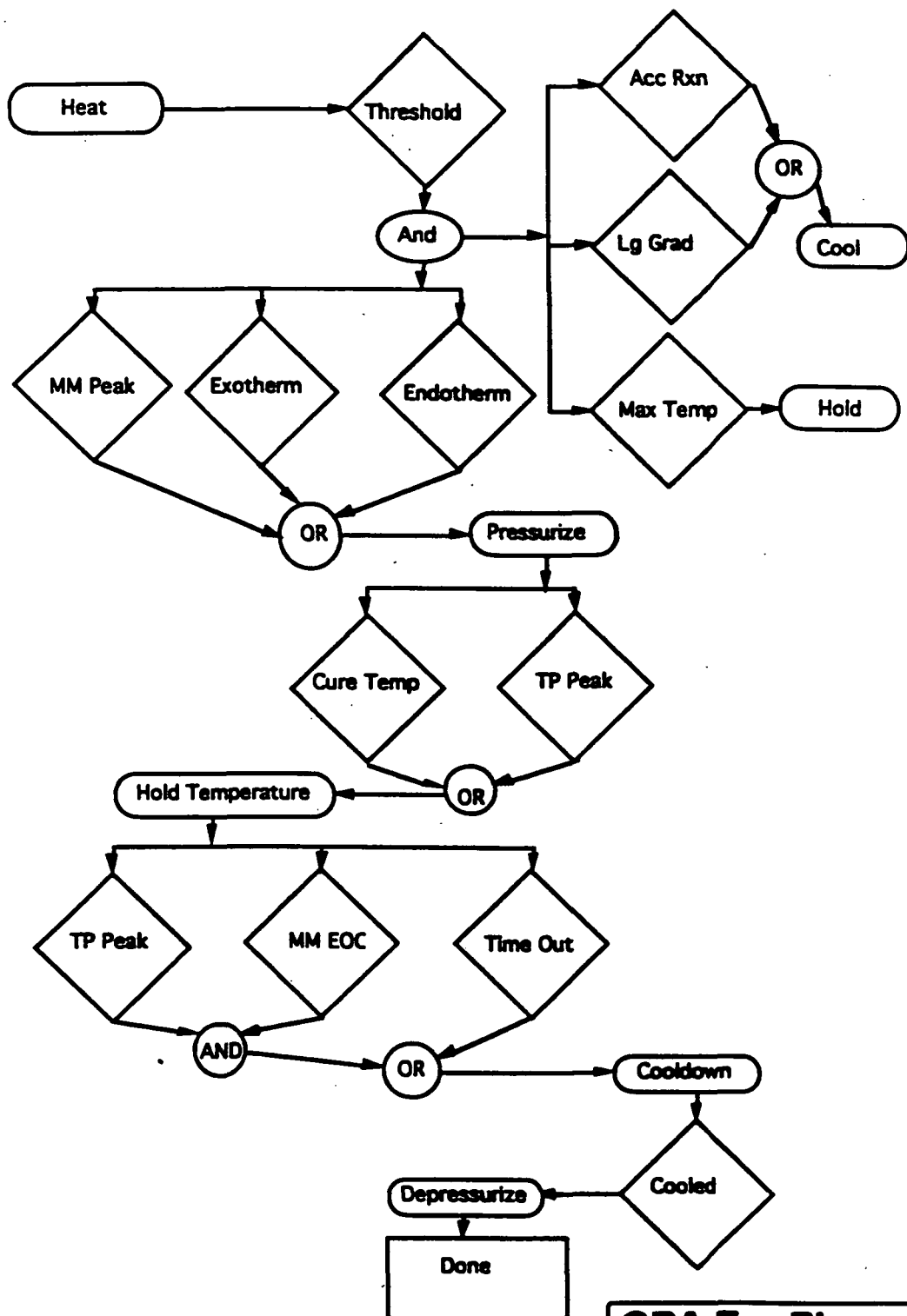
QPA For Phenolics
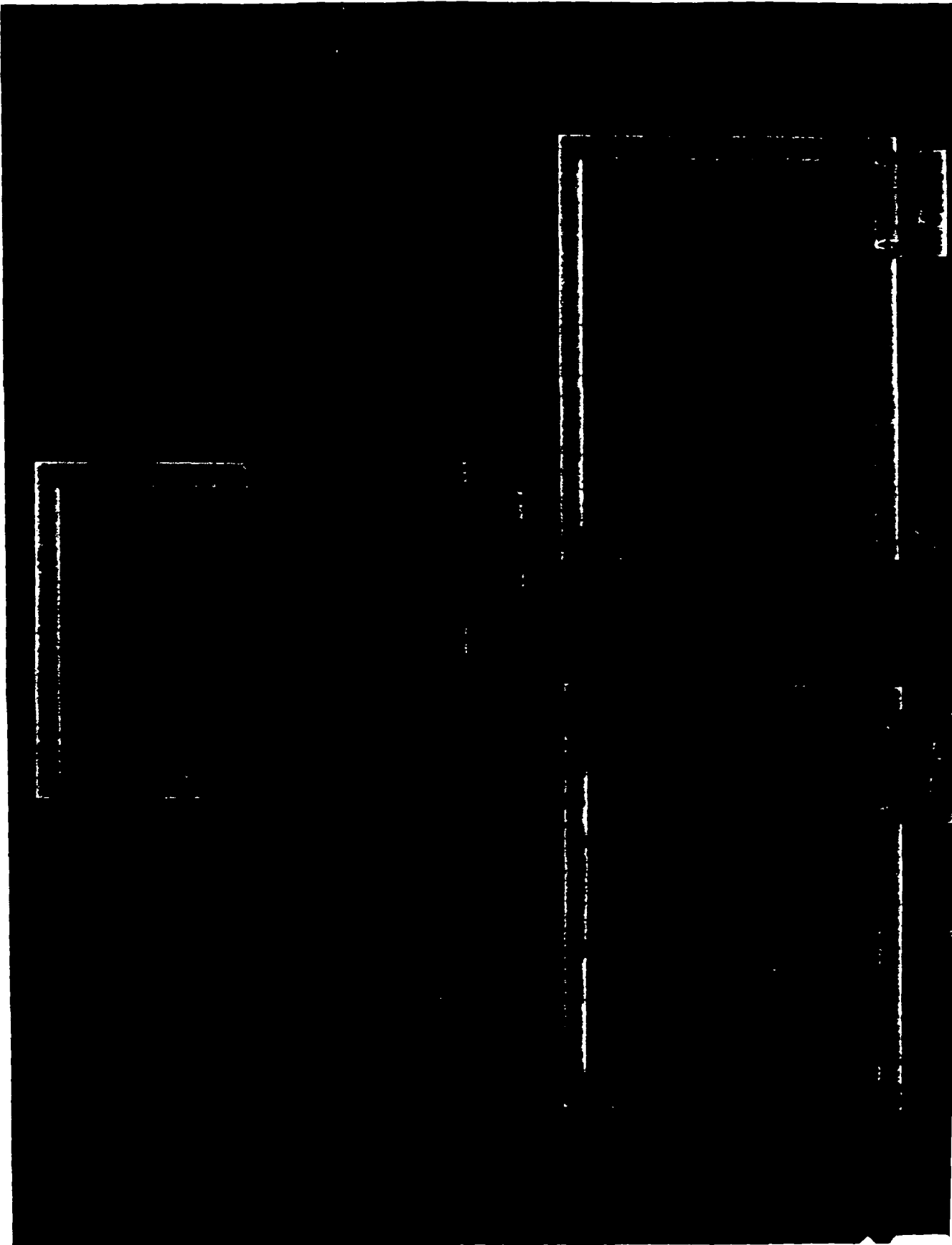
PROCESSING CHART FOR 140 PLIES BLISK
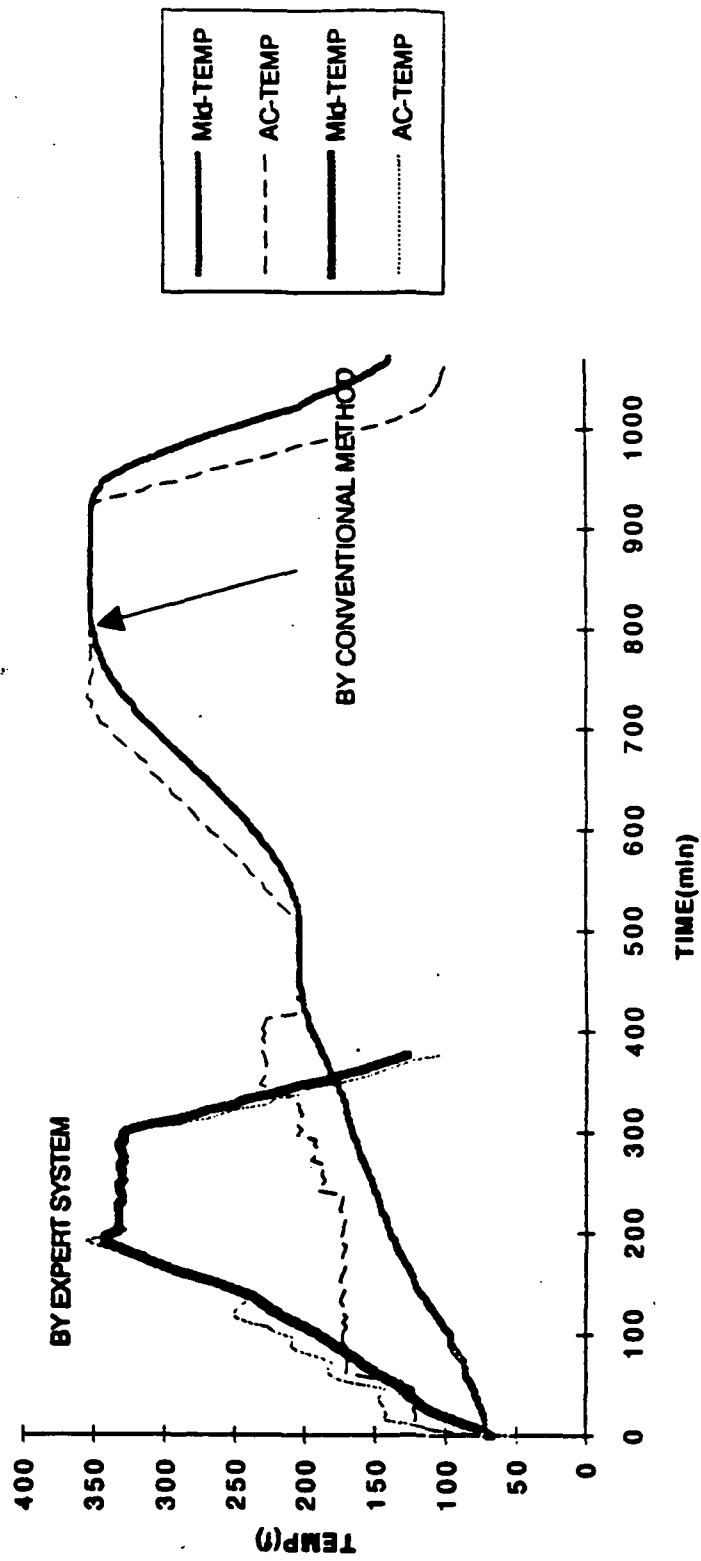
C-SCAN RESULTS

BY CONVENTIONAL METHOD
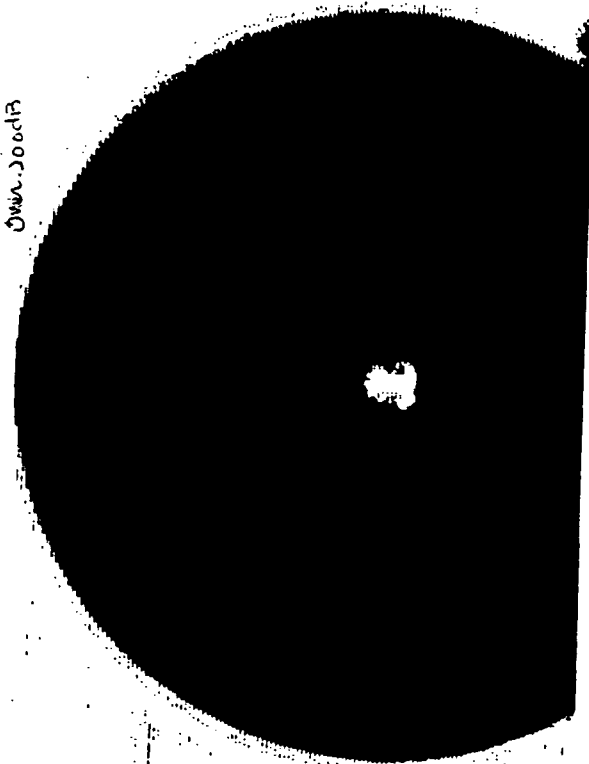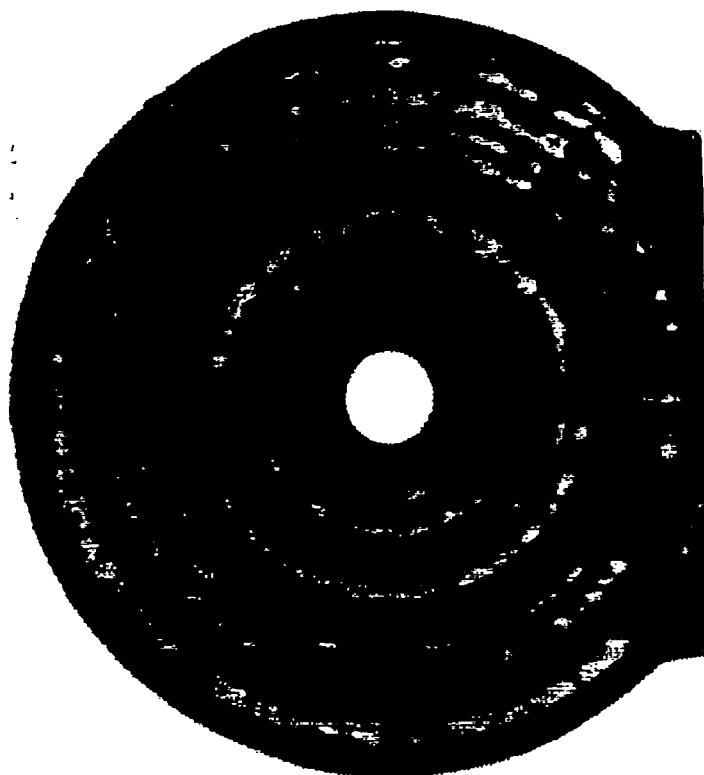
BY EXPERT SYSTEM

PHOTO-MICROGRAPHY

BY EXPERT SYSTEM
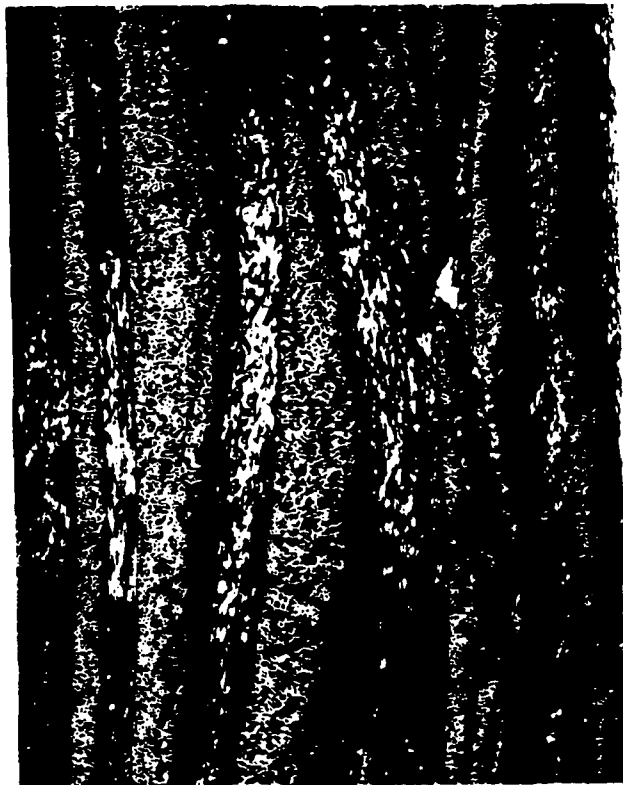
Expert Systems

Uses

Control of Batch Processes

Designer's Aids

   Exceptions

Limitations

Require Sensors and/or Models

Only as Good as Expertise & Information

Difficult to Verify

Artificial Neural Network (ANN)
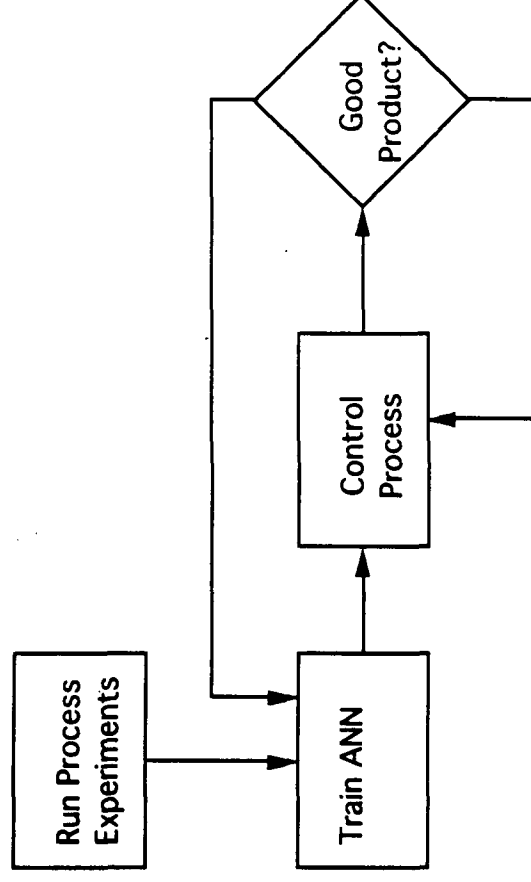
MANUFACTURING SCIENCE OF CARBON-CARBON STRUCTURES

SENSORS FOR PREPREG FILMING

Paper Thickness Sensor

Film/Paper Thickness Sensor

Film/Paper Beta Gauge

Paper Beta Gauge

Line Speed Sensor

Filler Consistency Sensor

Puddle Temperature

Color Sensor

Melt Pot Temperature

Chill Roll Temperature

Honeywell

C9031717
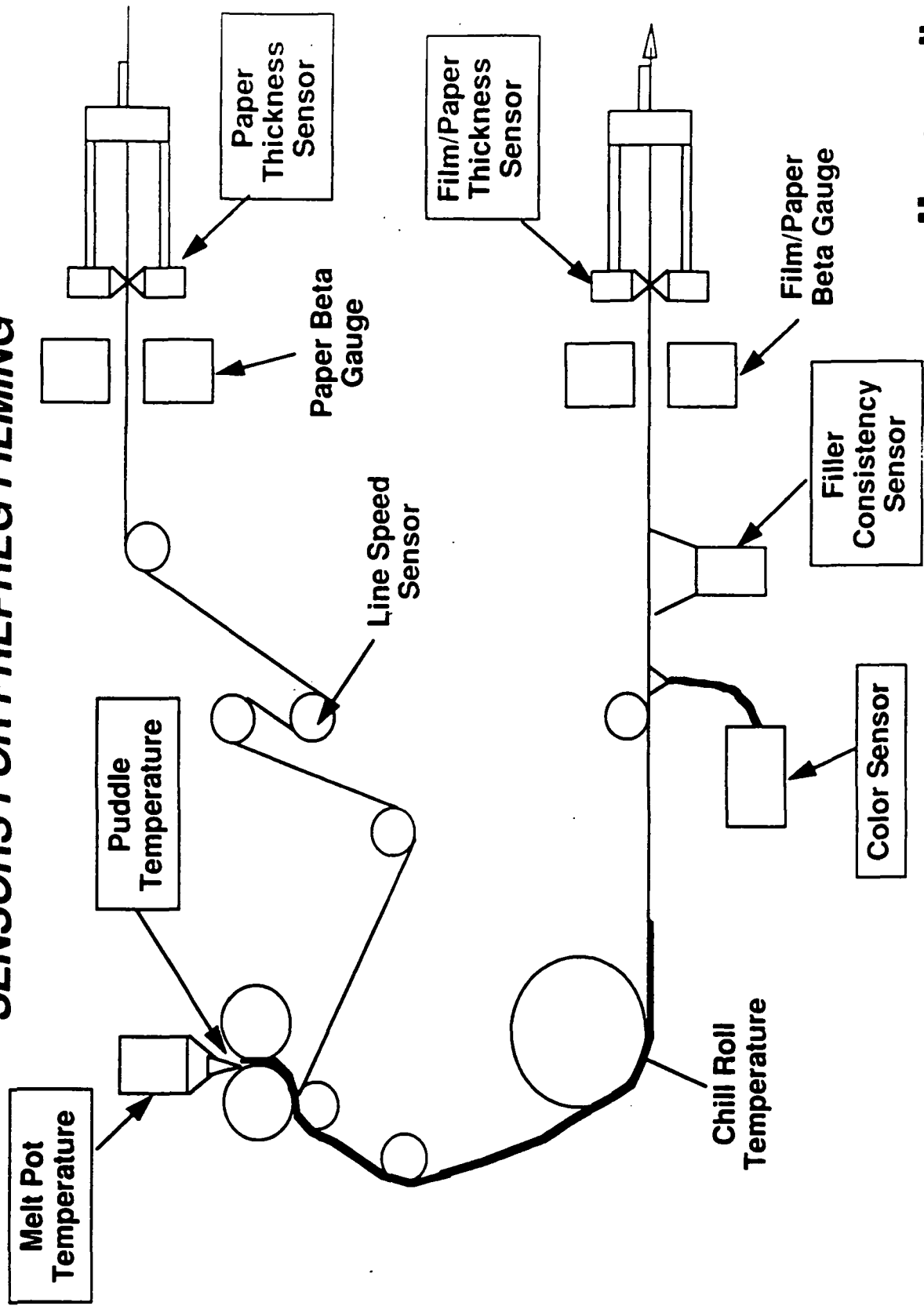
NEURAL NETWORK MODEL FOR FILMING PROCESS

Honeywell
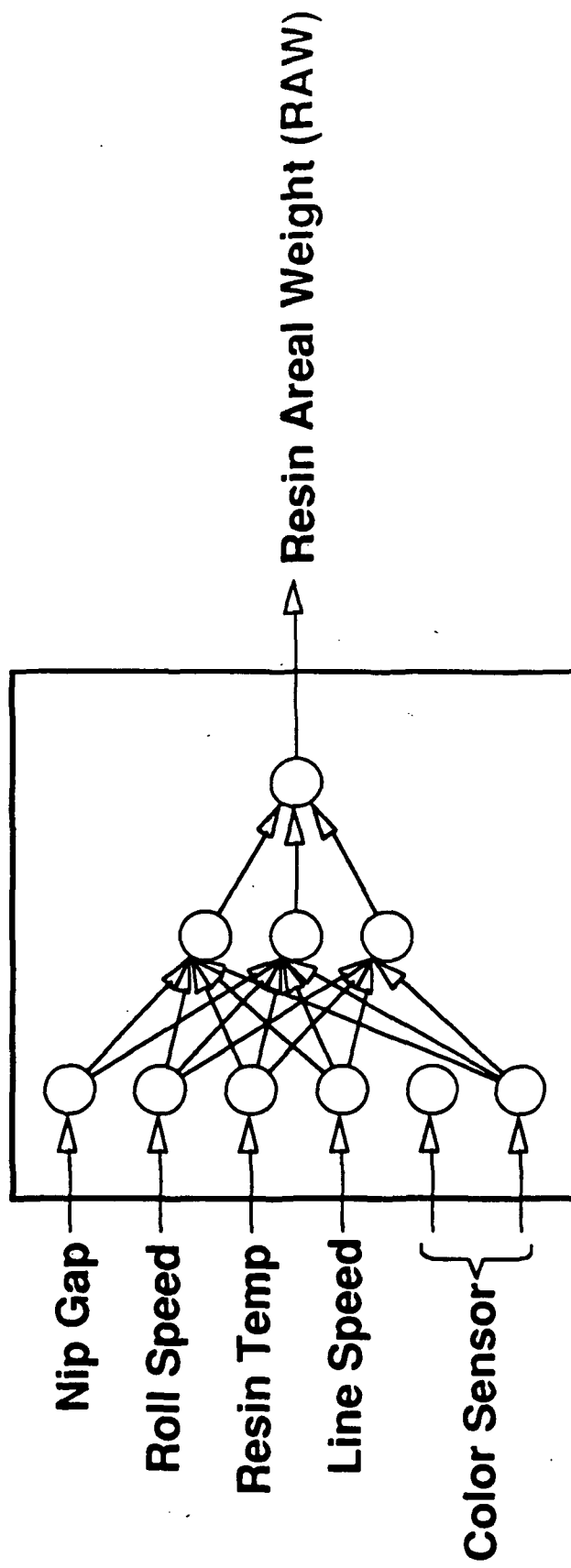
Improved Control of Prepreg with ANN Controller
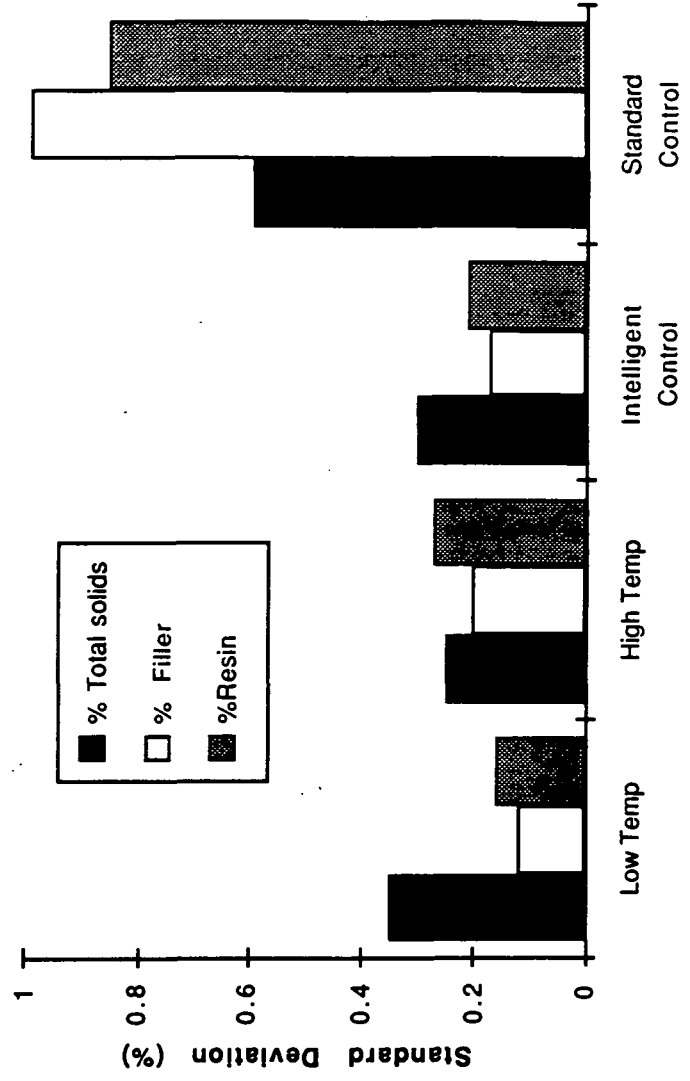
Artificial Neural Networks

Uses

Control of Continuous Processes

Pattern Recognition

Limitations

"Black Box"

Limited Number of Variables

Requires Training Set

Extrapolation may Fail
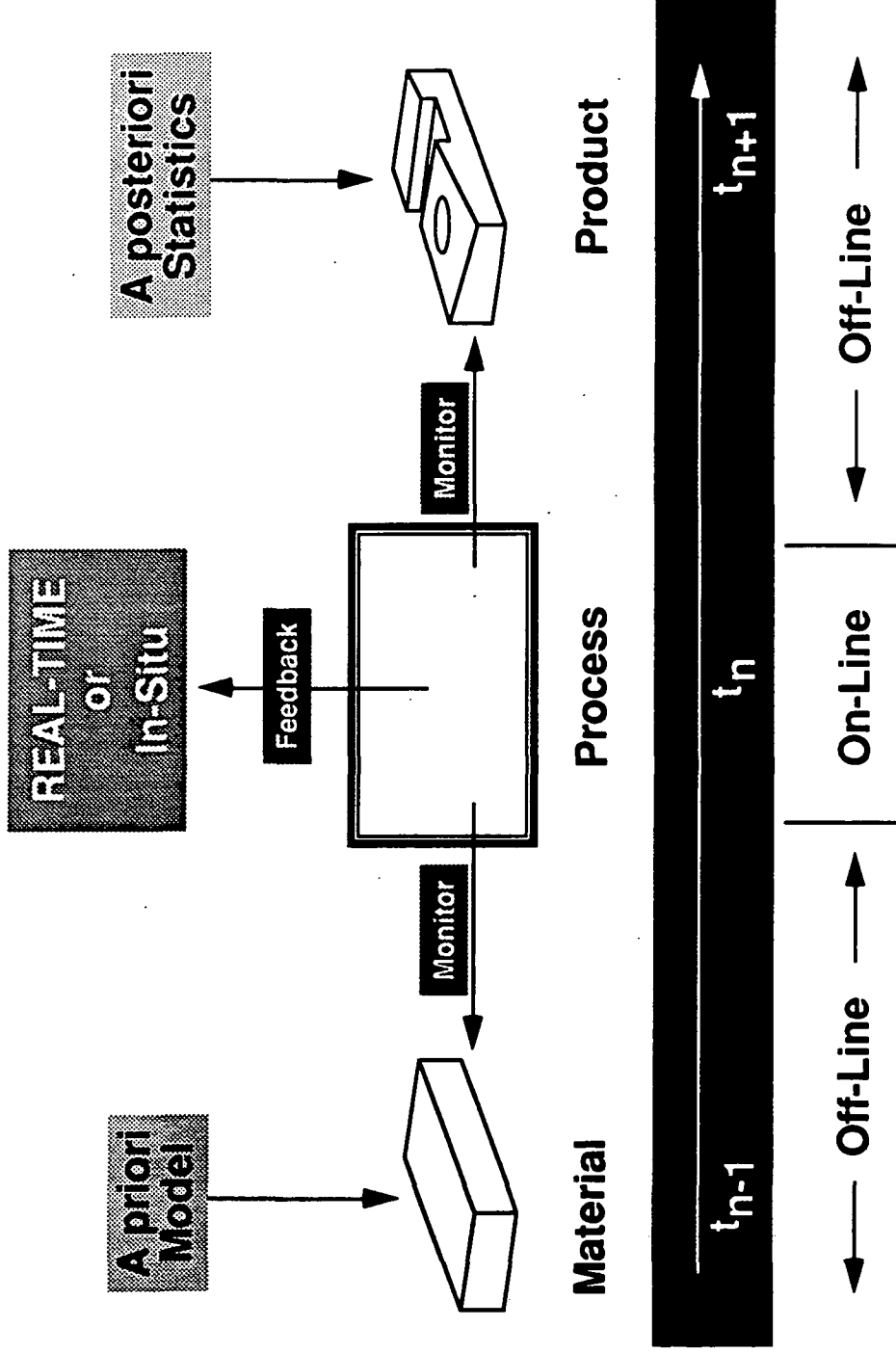
Apriori - REAL-TIME - Aposteriori Process Control Strategy

Cultural Change

A major barrier to improved manufacturing is non-technical.

"We can't afford it."

"It would require respecification."

"Not invented here"

"It doesn't pay to sell for less."

"No one else is doing it."

"None of our customers want us to."

In Conclusion

The Barrier to Improved Quality is not Technical

Tools are Available

Value is Demonstrated

Mindsets Have to Change

Fit The Tool to the Process

Improvement is Possible

Cost is Important

Appendix F—Personal Observations on Reliability of Shuttle

by R. P. Feynman.

It appears that there are enormous differences of opinion as to the probability of a failure with loss of vehicle and of human life. The estimates range from roughly 1 in 100 to 1 in 100,000. The higher figures come from working engineers, and the very low figures from management. What are the causes and consequences of this lack of agreement? Since 1 part in 100,000 would imply that one could put a Shuttle up each day for 300 years expecting to lose only one, we could more properly ask "What is the cause of management's fantastic faith in the machinery?"

We have also found that certification criteria used in Flight Readiness Reviews often develop a gradually decreasing strictness. The argument that the same risk was flown before without failure is often accepted as an argument for the safety of accepting it again. Because of this, obvious weaknesses are accepted again and again, sometimes without a sufficiently serious attempt to remedy them, or to delay a flight because of their continued presence.

There are several sources of information. There are published criteria for certification, including a history of modifications in the form of waivers and deviations. In addition, the records of the Flight Readiness Reviews for each flight document the arguments used to accept the risks of the flight. Information was obtained from the direct testimony and the reports of the range safety officer, Louis J. Ullian, with respect to the history of success of solid fuel rockets. There was a further study by him (as chairman of the launch abort safety panel (LASP)) in an attempt to determine the risks involved in possible accidents leading to radioactive contamination from attempting to fly a plutonium power supply (RTG) for future planetary missions. The NASA study of the same question is also available. For the history of the Space Shuttle Main Engines, interviews with management and engineers at Marshall, and informal interviews with engineers at Rocketdyne were made. An independent (Cal Tech) mechanical engineer who consulted for NASA about engines was also interviewed informally. A visit to Johnson was made to gather information on the reliability of the avionics (computers, sensors, and effectors). Finally there is a report "A Review of Certification Practices Potentially Applicable to Man-rated Reusable Rocket Engines," prepared at the Jet Propulsion Laboratory by N. Moore, et al., in February, 1986, for NASA Headquarters, Office of Space Flight. It deals with the methods used by the FAA and the military to certify their gas turbine and rocket engines. These authors were also interviewed informally.

Solid Fuel Rockets (SRB)

An estimate of the reliability of solid fuel rockets was made by the range safety officer, by studying the experience of all previous rocket flights. Out of a total of nearly 2,900 flights, 121 failed (1 in 25). This includes, however, what may be called, early errors, rockets flown for the first few times in which design errors are discovered and fixed. A more reasonable figure for the mature rockets might be 1 in 50. With special care in the selection of the parts and in inspection, a figure of below 1 in 100 might be achieved but 1 in 1,000 is probably not attainable with today's technology. (Since there are two rockets on the Shuttle, these rocket failure rates must be doubled to get Shuttle failure rates from Solid Rocket Booster failure.)

NASA officials argue that the figure is much lower. They point out that these figures are for unmanned rockets but since the Shuttle is a manned vehicle "the probability of mission success is necessarily very close to 1.0." It is not very clear what this phrase means. Does it mean it is close to 1 or that it ought to be close to 1? They go on to explain "Historically this extremely high degree of mission success has given rise to a difference in philosophy between manned space flight programs and unmanned programs; i.e., numerical probability usage versus engineering judgment." (These quotations are from "Space Shuttle Data for Planetary Mission RTG Safety Analysis," pages 3-1, 3-2, February 15, 1985, NASA, JSC.) It is true that if the probability of failure was as low as 1 in 100,000 it would take an inordinate number of tests to determine it (for you would get nothing but a string of perfect flights from which no precise figure, other than that the probability is likely less than the number of such flights in the string so far). But, if the real probability is not so small, flights would show troubles, near failures, and possibly actual failures with a reasonable number of trials, and standard statistical methods could give a reasonable estimate. In fact, previous NASA experience had shown, on occasion, just such difficulties, near accidents, and accidents, all giving warning that the probability of flight failure was not very small. The inconsistency of the argument not to determine reliability through historical experience, as the range safety officer did, is that NASA also appeals to history, beginning "Historically this high degree of mission success . . . ." Finally, if we are to replace standard numerical probability usage with engineering judgment, why do we find such an enormous disparity between the management estimate and the judgment of the engineers? It would appear that, for whatever purpose, be it for internal or external consumption, the management of NASA exaggerates the reliability of its product, to the point of fantasy.

The history of the certification and Flight Readiness Reviews will not be repeated here. (See other part of Commission reports.) The phenomenon of accepting for flight, seals that had shown erosion and blow-by in previous flights, is very clear. The Challenger flight is an excellent example. There are several references to flights, that had gone before. The acceptance and success of these flights is taken as evidence of safety. But erosion and blow-by are not what the design expected. They are warnings that something is wrong. The equipment is not operating as expected, and therefore there is a danger that it can operate with even wider deviations in this unexpected and not thoroughly understood way. The fact that this danger did not lead to a catastrophe before is no guarantee that it will not the next time, unless it is completely understood. When playing Russian roulette the fact that the first shot got off safely is little comfort for the next. The origin and consequences of the erosion and blow-by were not understood. They did not occur equally on all flights and all joints; sometimes more, and sometimes less. Why not sometime, when whatever conditions determined it were right, still more, leading to catastrophe?

In spite of these variations from case to case, officials behaved as if they understood it, giving apparently logical arguments to each other often depending on the "success" of previous flights. For example, in determining if flight 51-L was safe to fly in the face of ring erosion in flight 51-C, it was noted that the erosion depth was only one-third of the radius. It had been noted in an

term "safety factor." If a bridge is built to withstand a certain load
without the beams permanently deforming, cracking, or break-
ing, it may be designed for the materials used to actually stand
up under three times the load. This "safety factor" is to allow for
uncertain excesses of load, or unknown extra loads, or weaknesses
in the material that might have unexpected flaws, etc. If now the
expected load comes on to the new bridge and a crack appears
in a beam, this is a failure of the design. There was no safety
factor at all; even though the bridge did not actually collapse
because the crack only went one-third of the way through the
beam. The O-rings of the Solid Rocket Boosters were not designed
to erode. Erosion was a clue that something was wrong. Erosion
was not something from which safety can be inferred.

There was no way, without full understanding, that one could
have confidence that conditions the next time might not produce
erosion three times more severe than the time before. Never-
theless, officials fooled themselves into thinking they had such
understanding and confidence, in spite of the peculiar variations
from case to case. A mathematical model was made to calculate
erosion. This was a model based not on physical understanding
but on an empirical curve fitting. To be more detailed, it was sup-
posed a stream of hot gas impinged on the O-ring material, and
the heat was determined at the point of stagnation (so far, with
reasonable physical, thermodynamic laws). But to determine how
much rubber eroded it was assumed this depended only on this
heat by a formula suggested by data on a similar material. A
logarithmic plot suggested a straight line, so it was supposed that
the erosion varied as the .58 power of the heat, the .58 being deter-
mined by a nearest fit. At any rate, adjusting some other numbers,
it was determined that the model agreed with the erosion (to depth
of one-third the radius of the ring). There is nothing much so
wrong with this as believing the answer! Uncertainties appear
everywhere. How strong the gas stream might be was unpredict-
able, it depended on holes formed in the putty. Blow-by showed
that the ring might fail even though not, or only partially eroded
through. The empirical formula was known to be uncertain, for
it did not go directly through the very data points by which it
was determined. There were a cloud of points some twice above,
and some twice below the fitted curve, so erosions twice predicted
were reasonable from that cause alone. Similar uncertainties sur-
rounded the other constants in the formula, etc., etc. When using
a mathematical model careful attention must be given to uncer-
tainties in the model.

Liquid Fuel Engine (SSME)

During the flight of 51-L the three Space Shuttle Main Engines
all worked perfectly, even, at the last moment, beginning to shut
down the engines as the fuel supply began to fail. The question
arises, however, as to whether, had it failed, and we were to in-
vestigate it in as much detail as we did the Solid Rocket Booster,
we would find a similar lack of attention to faults and a
deteriorating reliability. In other words, were the organization
weaknesses that contributed to the accident confined to the Solid
Rocket Booster sector or were they a more general characteristic
of NASA? To that end the Space Shuttle Main Engines and the
avionics were both investigated. No similar study of the Orbiter,
or the External Tank was made.

The engine is a much more complicated structure than the Solid
Rocket Booster, and a great deal more detailed engineering goes
into it. Generally, the engineering seems to be of high quality

...and apparently considerable attention is paid to deficiencies and
faults found in operation.

The usual way that such engines are designed (for military or
civilian aircraft) may be called the component system, or bottom-
up design. First it is necessary to thoroughly understand the prop-
erties and limitations of the materials to be used (for turbine
blades, for example), and tests are begun in experimental rigs
to determine those. With this knowledge larger component parts
(such as bearings) are designed and tested individually. As defi-
ciencies and design errors are noted they are corrected and verified
with further testing. Since one tests only parts at a time these
tests and modifications are not overly expensive. Finally one works
up to the final design of the entire engine, to the necessary
specifications. There is a good chance, by this time that the engine
will generally succeed, or that any failures are easily isolated and
analyzed because the failure modes, limitations of materials, etc.,
are so well understood. There is a very good chance that the
modifications to the engine to get around the final difficulties are
not very hard to make, for most of the serious problems have
already been discovered and dealt with in the earlier, less expen-
sive, stages of the process.

The Space Shuttle Main Engine was handled in a different
manner, top down, we might say. The engine was designed and
put together all at once with relatively little detailed preliminary
study of the material and components. Then when troubles are
found in the bearings, turbine blades, coolant pipes, etc., it is
more expensive and difficult to discover the causes and make
changes. For example, cracks have been found in the turbine
blades of the high pressure oxygen turbopump. Are they caused
by flaws in the material, the effect of the oxygen atmosphere on
properties of the material, the thermal stresses of startup or shut-
down, the vibration and stresses of steady running, or mainly
at some resonance at certain speeds, etc.? How long can we run
from crack initiation to crack failure, and how does this depend
on power level? Using the completed engine as a test bed to resolve
such questions is extremely expensive. One does not wish to lose
entire engines in order to find out where and how failure occurs.
Yet, an accurate knowledge of this information is essential to ac-
quire a confidence in the engine reliability in use. Without detailed
understanding, confidence cannot be attained.

A further disadvantage of the top-down method is that, if an
understanding of a fault is obtained, a simple fix, such as a new
shape for the turbine housing, may be impossible to implement
without a redesign of the entire engine.

The Space Shuttle Main Engine is a very remarkable machine.
It has a greater ratio of thrust to weight than any previous engine.
It is built at the edge of, or outside of, previous engineering ex-
perience. Therefore, as expected, many different kinds of flaws
and difficulties have turned up. Because, unfortunately, it was
built in the top-down manner, they are difficult to find and to
fix. The design aim of a lifetime of 55 mission equivalent firings
(27,000 seconds of operation, either in a mission of 500 seconds,
or on a test stand) has not been obtained. The engine now re-
quires very frequent maintenance and replacement of important
parts, such as turbopumps, bearings, sheet metal housings, etc.
The high-pressure fuel turbopump had to be replaced every three
or four mission equivalents (although that may have been fixed,
now) and the high-pressure oxygen turbopump every five or six.
This is at most ten percent of the original specification. But our
main concern here is the determination of reliability.

In a total of about 250,000 seconds of operation, the engines
have failed seriously perhaps 16 times. Engineering pays close
attention to these failings and tries to remedy them as quickly
as possible. This it does by test studies on special rigs experimen-
tally designed for the flaw in question, by careful inspection of
the engine for suggestive clues (like cracks), and by considerable
study and analysis. In this way, in spite of the difficulties of top-
down design, through hard work, many of the problems have ap-
parently been solved.

- Turbine blade cracks in high-pressure fuel turbopumps (HPFTP). (May have been solved.)
- Turbine blade cracks in high-pressure oxygen turbopumps (HPOTP).
- Augmented Spark Igniter (ASI) line rupture. *
- Purge check valve failure. *
- ASI chamber erosion. *
- HPFTP turbine sheet metal cracking.
- HPFTP coolant liner failure. *
- Main combustion chamber outlet elbow failure. *
- Main combustion chamber inlet elbow weld offset. *
- HPOTP subsynchronous whirl. *
- Flight acceleration safety cutoff system (partial failure in a redundant system). *
- Bearing spalling (partially solved).
- A vibration at 4,000 Hertz making some engines inoperable. etc.

Many of these solved problems are the early difficulties of a new design, for 13 of them occurred in the first 125,000 seconds and only three in the second 125,000 seconds. Naturally, one can never be sure that all the bugs are out, and, for some, the fix may not have addressed the true cause. Thus, it is not unreasonable to guess there may be at least one surprise in the next 250,000 seconds, a probability of 1/500 per engine per mission. On a mission there are three engines, but some accidents would possibly be contained, and only affect one engine. The system can abort with only two engines. Therefore let us say that the unknown surprises do not, even of themselves, permit us to guess that the probability of mission failure due to the Space Shuttle Main Engine is less than 1/500. To this we must add the chance of failure from known, but as yet unsolved, problems (introduced by asterisk in the list above). These we discuss below. (Engineers at Rocketdyne, the manufacturer, estimate the total probability as 1/10,000. Engineers at Marshall estimate it as 1/300, while NASA management, to whom these engineers report, claims it is 1/100,000. An independent engineer consulting for NASA thought 1 or 2 per 100 a reasonable estimate.)

The history of the certification principles for these engines is confusing and difficult to explain. Initially the rule seems to have been that two sample engines must each have had twice the time operating without failure, as the operating time of the engine to be certified (rule of 2x). At least that is the FAA practice, and NASA seems to have adopted it, originally expecting the certified time to be 10 missions (hence 20 missions for each sample). Obviously the best engines to use for comparison would be those of greatest total (flight plus test) operating time—the so-called "fleet leaders." But what if a third sample and several others fail in a short time? Surely we will not be safe because two were unusual in lasting longer. The short time might be more representative of the real possibilities, and in the spirit of the safety factor of 2, we should only operate at half the time of the short-lived samples.

The slow shift toward decreasing safety factor can be seen in many examples. We take that of the HPFTP turbine blades. First of all the idea of testing an entire engine was abandoned. Each engine number has had many important parts (like the turbopumps themselves) replaced at frequent intervals, so that the rule must be shifted from engines to components. We accept an HPFTP for a certification time if two samples have each run successfully for twice that time (and of course, as a practical matter, no longer insisting that this time be as large as 10 missions). But what is "successfully"? The FAA calls a turbine blade crack a failure, in order, in practice, to really provide a safety factor greater than 2. There is some time that an engine can run between the time a crack originally starts until the time it has grown large enough to fracture. (The FAA is contemplating new rules that take this extra safety time into account, but only if it is very

carefully analyzed through known models within a known range of experience and with materials thoroughly tested. None of these conditions apply to the Space Shuttle Main Engine.

Cracks were found in many second stage HPFTP turbine blades. In one case three were found after 1,900 seconds, while in another they were not found after 4,200 seconds, although usually these longer runs showed cracks. To follow this story further we shall have to realize that the stress depends a great deal on the power level. The Challenger flight was to be at, and previous flights had been at, a power level called 104% of rated power level during most of time the engines were operating. Judging from some material data it is supposed that at the level 104% of rated power level, the time to crack is about twice that at 109% or full power level (FPL). Future flights were at this level because of heavier payloads, and many tests were made at this level. Therefore dividing time at 104% by two, we obtain units called equivalent full power level (EFPL). (Obviously, some uncertainty is introduced by that, but it has not been studied.) The earliest cracks mentioned above occurred at 1,375 EFPL.

Now the certification rule becomes "limit all second stage blades to a maximum of 1,375 seconds EFPL." If one objects that the factor of 2 is lost it is pointed out that the one turbine ran for 3,800 seconds EFPL without cracks, and half of this is 1,900 so we are being more conservative. We have fooled ourselves in three ways. First we have only one sample, and it is not the fleet leader, for the other two samples of 3,800 or more seconds had 17 cracked blades between them. (There are 59 blades in the engine.) Next we have abandoned the 2x rule and substituted equal time. And finally, 1,375 is where we did see a crack. We can say that no crack had been found below 1,375, but the last time we looked and saw no cracks was 1,100 seconds EFPL. We do not know when the crack formed between these times, for example cracks may have formed at 1,150 seconds EFPL. (Approximately ⅔ of the blade sets tested in excess of 1,375 seconds EFPL had cracks. Some recent experiments have, indeed, shown cracks as early as 1,150 seconds.) It was important to keep the number high, for the Challenger was to fly an engine very close to the limit by the time the flight was over.

Finally it is claimed that the criteria are not abandoned, and the system is safe, by giving up the FAA convention that there should be no cracks, and considering only a completely fractured blade a failure. With this definition no engine has yet failed. The idea is that since there is sufficient time for a crack to grow to fracture we can insure that all is safe by inspecting all blades for cracks. If they are found, replace them, and if none are found we have enough time for a safe mission. This makes the crack problem not a flight safety problem, but merely a maintenance problem.

This may in fact be true. But how well do we know that crack always grow slowly enough that no fracture can occur in a mission? Three engines have run for long times with a few cracked blades (about 3,000 seconds EFPL) with no blades broken off.

But a fix for this cracking may have been found. By changing the blade shape, shot-peening the surface, and covering with insulation to exclude thermal shock, the blades have not cracked so far.

A very similar story appears in the history of certification of the HPOTP, but we shall not give the details here.

It is evident, in summary, that the Flight Readiness Reviews and certification rules show a deterioration for some of the problems of the Space Shuttle Main Engine that is closely analogous to the deterioration seen in the rules for the Solid Rocket Booster.

Avionics

By "avionics" is meant the computer system on the Orbiter as well as its input sensors and output actuators. At first we will restrict ourselves to the computers proper and not be concerned with the reliability of the input information from the sensors of

temperature, pressure, etc., or with whether the computer put-
... is correctly allowed ... the actuators of rocket firings,
mechanical controls, also ... to astronauts, etc.

The computing system is ... elaborate, having over 250,000
lines of code. It is responsible, among many other things, for the
automatic control of the entire ascent to orbit, and for the de-
scent until well into the atmosphere (below Mach 1) once one
button is pushed deciding the landing site desired. It would be
possible to make the entire landing automatically (except that the
landing gear lowering signal is expressly left out of computer con-
trol, and must be provided by the pilot, ostensibly for safety
reasons) but such an entirely automatic landing is probably not
as safe as a pilot controlled landing. During orbital flight it is
used in the control of payloads, in displaying information to the
astronauts, and the exchange of information to the ground. It
is evident that the safety of flight requires guaranteed accuracy
of this elaborate system of computer hardware and software.

In brief, the hardware reliability is ensured by having four
essentially independent identical computer systems. Where possi-
ble each sensor also has multiple copies, usually four, and each
copy feeds all four of the computer lines. If the inputs from the
sensors disagree depending on circumstances certain averages,
or a majority selection is used as the effective input. The algorithm
used by each of the four computers is exactly the same, so their
inputs (since each sees all copies of the sensors) are the same.
Therefore at each step the results in each computer should be
identical. From time to time they are compared, but because they
might operate at slightly different speeds a system of stopping
and waiting at specified times is instituted before each comparison
is made. If one of the computers disagrees, or is too late in hav-
ing its answer ready, the three which do agree are assumed to
be correct and the errant computer is taken completely out of the
system. If, now, another computer fails, as judged by the agree-
ment of the other two, it is taken out of the system, and the rest
of the flight canceled, and descent to the landing site is instituted,
controlled by the two remaining computers. It is seen that this
is a redundant system since the failure of only one computer does
not affect the mission. Finally, as an extra feature of safety, there
is a fifth independent computer, whose memory is loaded with
only the programs for ascent and descent, and which is capable
of controlling the descent if there is a failure of more than two
of the computers of the main line of four.

There is not enough room in the memory of the main line com-
puters for all the programs of ascent, descent, and payload pro-
grams in flight, so the memory is loaded about four times from
tapes, by the astronauts.

Because of the enormous effort required to replace the soft-
ware for such an elaborate system, and for checking a new system
out, no change has been made in the hardware since the system
began about fifteen years ago. The actual hardware is obsolete;
for example, the memories are of the old ferrite core type. It is
becoming more difficult to find manufacturers to supply such old-
fashioned computers reliably and of high quality. Modern com-
puters are very much more reliable, can run much faster, simpli-
fying circuits, and allowing more to be done, and would not re-
quire so much loading of memory, for their memories are much
larger.

The software is checked very carefully in a bottom-up fashion.
First, each new line of code is checked, then sections of codes
or modules with special function are verified. The scope is in-
creased step by step until the new changes are incorporated into
a complete system and checked. This complete output is con-
sidered the final product, newly released. But completely in-
dependently there is an independent verification group, that takes
an adversary attitude to the software development group, and
tests and verifies the software as if it were a customer of a delivered
product. There is additional verification in using the new pro-
grams in simulators, etc. A discovery of an error during the
verification testing is considered very serious, and its origin studied
very carefully to avoid such mistakes in the future. Such unex-

pected errors have been found only about six times ... the pro-
gramming and program changing (for new or altered payloads)
that has been done. The principle that is followed ... at all the
verification is not an aspect of program safety, merely a test
of that safety, in a non-catastrophic verification flight safety is
to be judged solely on how well the programs do in the verifica-
tion tests. A failure here generates considerable concern.

To summarize then, the computer software checking system
and attitude is of highest quality. There appears to be no process
of gradually fooling oneself while degrading standards so
characteristic of the Solid Rocket Booster or Space Shuttle Main
Engine safety systems. To be sure, there have been recent sug-
gestions by management to curtail such elaborate and expensive
tests as being unnecessary at this late date in Shuttle history. This
must be resisted for it does not appreciate the mutual subtle in-
fluences, and sources of error generated by even small changes
on one part of a program on another. There are perpetual re-
quests for changes as new payloads and new demands and
modifications are suggested by the users. Changes are expensive
because they require extensive testing. The proper way to save
money is to curtail the number of requested changes, not the quali-
ty of testing for each.

One might add that the elaborate system could be very much
improved by more modern hardware and programming tech-
niques. Any outside competition would have all the advantages
of starting over, and whether that is a good idea for NASA now
should be carefully considered.

Finally, returning to the sensors and actuators of the avionics
system, we find that the attitude to system failure and reliability
is not nearly as good as for the computer system. For example,
a difficulty was found with certain temperature sensors sometimes
failing. Yet 18 months later the same sensors were still being used,
still sometimes failing, until a launch had to be scrubbed because
two of them failed at the same time. Even on a succeeding flight
this unreliable sensor was used again. Again reaction control
systems, the rocket jets used for reorienting and control in flight,
still are somewhat unreliable. There is considerable redundan-
cy, but a long history of failures, none of which has yet been ex-
tensive enough to seriously affect a flight. The action of the jets
is checked by sensors, and, if they fail to fire the computers choose
another jet to fire. But they are not designed to fail, and the prob-
lem should be solved.

Conclusions

If a reasonable launch schedule is to be maintained, engineer-
ing often cannot be done fast enough to keep up with the expec-
tations of originally conservative certification criteria designed
to guarantee a very safe vehicle. In these situations, subtly, and
often with apparently logical arguments, the criteria are altered
so that flights may still be certified in time. They therefore fly
in a relatively unsafe condition, with a chance of failure of the
order of a percent (it is difficult to be more accurate).

Official management, on the other hand, claims to believe the
probability of failure is a thousand times less. One reason for this
may be an attempt to assure the government of NASA perfec-
tion and success in order to ensure the supply of funds. The other
may be that they sincerely believe it to be true, demonstrating
an almost incredible lack of communication between themselves
and their working engineers.

In any event this has had very unfortunate consequences, the
most serious of which is to encourage ordinary citizens to fly in
such a dangerous machine, as if it had attained the safety of an
ordinary airliner. The astronauts, like test pilots, should know
their risks, and we honor them for their courage. Who can doubt
that McAuliffe was equally a person of great courage, who was
closer to an awareness of the true risk than NASA management
would have us believe?

F-4

make recommendations to ensure that NASA officials a world of reality in understanding technological issues and imperfections well enough to be actively trying to abate them. They must live in reality in comparing the cost and utility of the Shuttle to other methods of entering space. They must be realistic in making contracts, in estimating costs, and the difficulty of the projects. Only realistic flight schedules should be proposed, schedules that have a reasonable chance of being met. If in this way the government would not support them, then so be it. NASA owes it to the citizens from whom it asks support to be frank, honest, and informative, so that these citizens can make the wisest decisions for the use of their limited resources.

For a successful technology, reality must take precedence over public relations, for nature cannot be fooled.

Round-robin Permeability Testing Status

MSFC Qualification of ASTM D1434 Permeability Test

SPIP 3.2.1.1 Industry Meeting

Mississippi State University

Starkville, Mississippi

18 - 19 May 1994

A. J. Day

Thiokol Huntsville Space Operations

Specimens for Permeability Round Robin Testing

The following Aft Exit Cone tag end specimens have been identified as candidates for round robin testing of permeability between SRI, MSFC, and PMI. All specimens are fill direction samples.

Serial Number (S/N)	Flight	SRI permeability
S/N 7 Fwd	TEM-10	-13.74
S/N 75 Fwd	TEM-9	-17.5
S/N 75 Aft	TEM-9	-13.91
*S/N 76 Aft	21A	-14.84
S/N 78 Fwd	31A	-15.03
S/N 95 Fwd	29B	-14.15
S/N 112 Aft	36B	-15.57
S/N 113 Aft	37B	-17.20
S/N 114 Fwd	37A	-16.53
S/N 115 Aft	39B	-16.50
S/N 118 Aft	40B	-15.94
S/N 120 Aft	41B	-14.98
S/N 121 Fwd	42A	-15.94
Graphite Phenolic	E. T. Nose Cap	-------
2219 Aluminum	----	-------

* S/N 76 Aft AEC tag end not tested due to specimen size.

In addition, to test the upper and lower range of the test facilities, a specimen of graphite phenolic (Darcy = -9.6) and Aluminum (Darcy = -20) will also be tested.

Proposed Permeabilit, Range of Test

SRI Tested Values

Specimen Serial Number
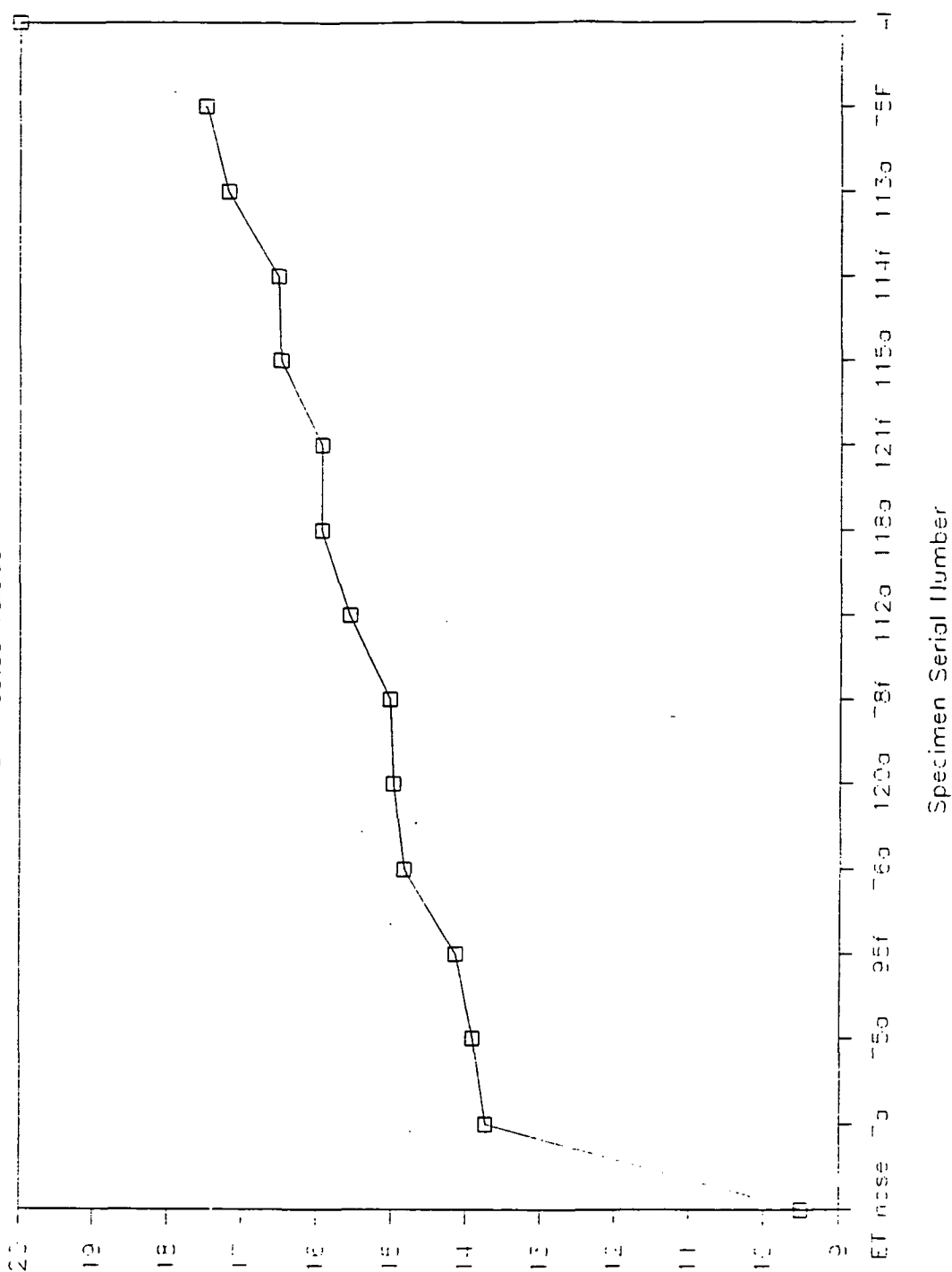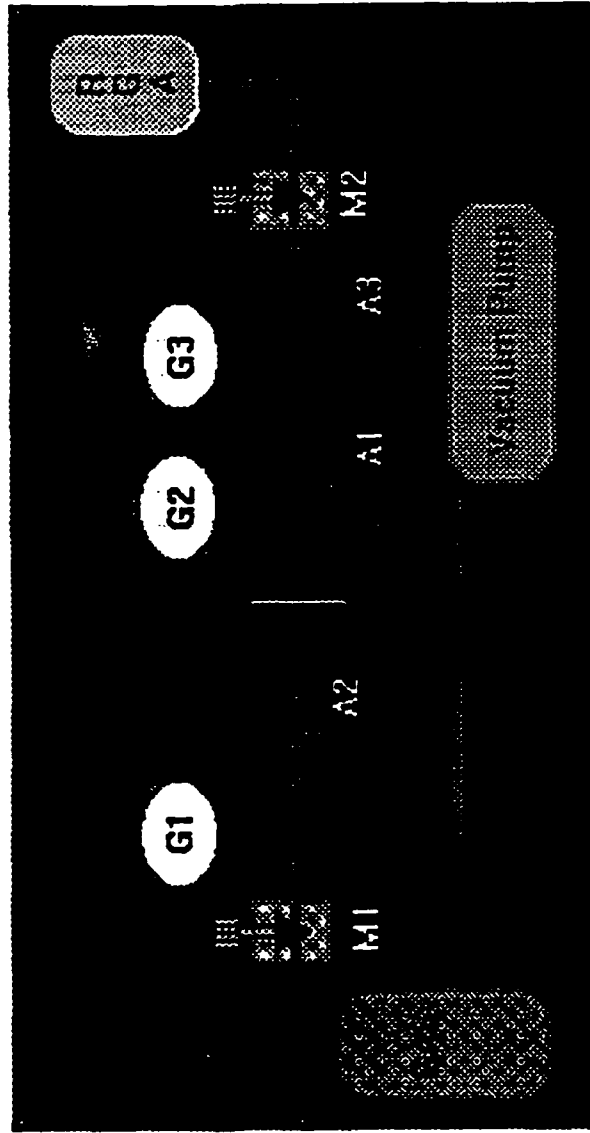
PMI Residual Gas Analyzer (RGA) Schematic
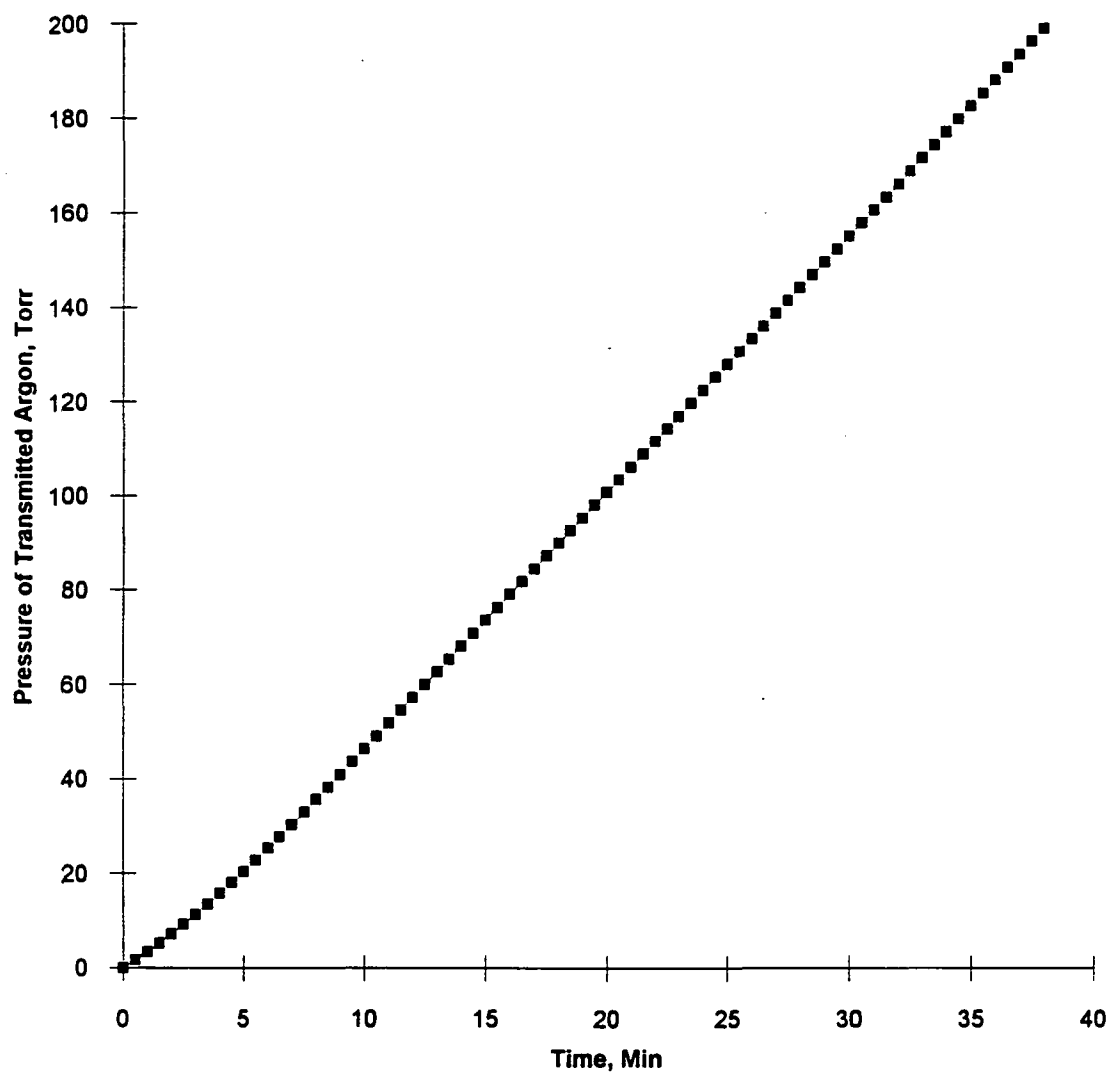
RGA Results

The results of the PMI RGA testing on the nine specimens are listed here. For comparison, the MSFC and SRI values are tabulated also.

Permeability of Round-Robin Specimens

Specimen	PMI RGA Value	MSFC Value	SRI Value
S/N 75 Aft	-15.17	-13.87	-13.91
S/N 78 Fwd	-15.38	-15.02	-15.03
S/N 95 Fwd	-15.68	-14.12	-14.15
S/N 113 Aft	-17.35	-17.32	-17.20
S/N 114 Fwd	-15.34	-16.78	-16.53
S/N 115 Aft	-15.66	-16.61	-16.50
S/N 118 Aft	-15.65	-15.97	-15.94
S/N 120 Aft	-16.04	-15.27	-14.98
S/N 121 Fwd	-15.47	-15.67	-15.94

The comparison of results between the three round-robin participants is reasonable. MSFC and SRI compare very closely, with PMI not being as close. However, it is premature to make final evaluations on the PMI results because these are single tests on single specimens and it is not possible to judge the reproducibility of the test until replicates are performed. Also, the remainder of the round-robin has yet to be completed. The second part of the round-robin will be completed in the upcoming quarter.

In the course of testing, it became apparent that the ASTM D1434 test cell had to be further modified in order to give the desired reproducible results. In the previous quarter the following modifications had been accomplished:

1. Specimens sizes had been modified from the 0.95 inch diameter, 0.115 inch thick size to a 1 inch diameter, 0.25 inch thick "standard" SRI size of specimen. This eliminated extra machining of specimens.

2. Aluminum specimen plates to hold the new specimen size were fabricated.

3. Glass precision bore capillary tubes of a range of sizes were obtained. This allows the flow of permeating gas to be accurately collected from specimens with a wide range of permeabilities. The capillary tubes have sizes of 0.1, 0.25, 0.5, 2.0 and 3.0 millimeter diameters. These helped speed the test by decreasing the amount of gas required to accurately measure permeability.

4. The test procedure was modified to allow the use of permeating gas pressures up to 30 psig. This speeds the measurements for very low permeability specimens by increasing the flow of permeating gas through the specimen.

5. Eliminated the water bath called for by ASTM D1434.

6. Purchased "permeability standards". Poretics Corporation polycarbonate track-etched filters of known pore size and distribution.

7. Eliminated the use of vacuum grease for sealing O-rings to specimens.

Permeability Test Development

D 1434

Gas Pressure
Double Stage
Regulator

Gas
Inlet

Pressure
Valve

Constant
Temperature
Bath

Drying
Column

Oil Traps
(Bubblers)

Capillary
Tube

2 Filter Papers

Specimen

Teflon
Gasket

Heat
Exchanger

To
Manometer
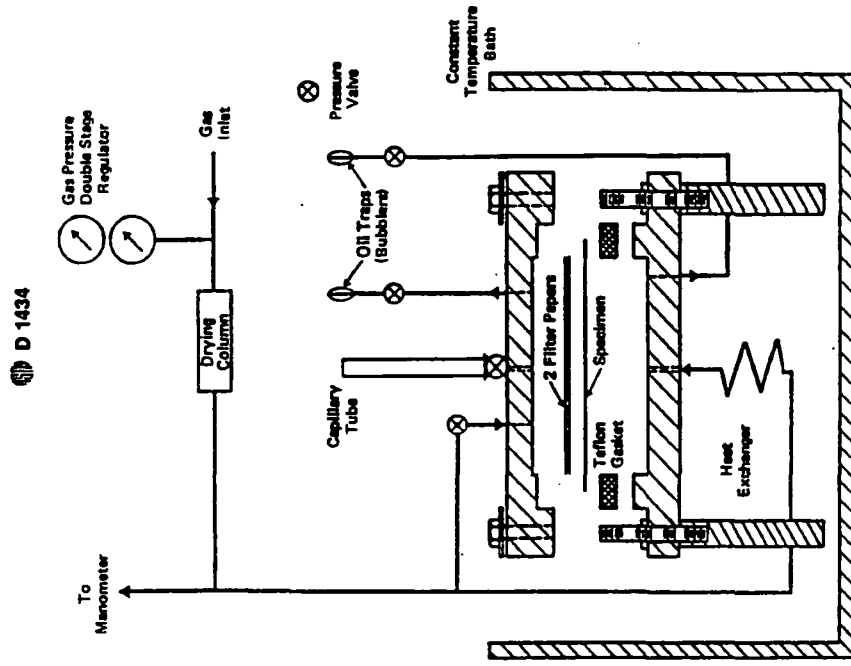
ASTM D1434 Volumetric Gas Transmission Cell Schematic
"Linde Cell"

Some data typical of the problems encountered before removing the water bath are tabulated here.

Multiple Analysis of A Single Specimen
Using ASTM D1434 with Water Bath
S/N 78 F AEC Tag End

Series 1

Analysis Time (Seconds)	Flow Rate (cc/sec)	Permeability (Darcy Units)
16	6.136e-5	-15.39
23	4.268e-5	-15.55
18		-15.44
25	3.927e-5	-15.59
		Avg = -15.49, s = 0.093

Series 2

20	4.909e-5	-15.48
21	4.675e-5	-15.51
25	3.927e-5	-15.59
19	5.167e-5	-15.47
		Avg = -15.51, s = 0.054

Series 3

30	4.909e-5	-15.49
36	4.091e-5	-15.57
37	3.980e-5	-15.58
35	4.207e-5	-15.56
		Avg = -15.55, s = 0.041

Series 4 (1 hour delay)

22	4.462e-5	-15.53
32	3.068e-5	-15.69
32	3.068e-5	-15.69
35	2.805e-5	-15.73
35	2.805e-5	-15.73
		Avg = -15.67, s = 0.083

Series 5

64 (2 reps)	2.301e-5	-15.82
82	1.796e-5	-15.93
89	1.655e-5	-15.96
		Avg = -15.88, s = 0.073

Overall average permeability = -15.615
Overall average standard deviation = 0.156

Highest value reported was the first result. Lowest value reported was the last result. The specimen appeared to be becoming less permeable with time.

The initial interpretation of these results was that the test apparatus was leaking water (which lowers the permeability) or the O-ring holding the specimen was excessively compressed due to hand torquing the wing nuts.

Multiple Analysis of A Single Specimen
Without Water Bath
S/N 78 F AEC Tag End

Series 1

Analysis Time (Seconds)	Flow Rate (cc/sec)	Permeability (Darcy Units)
48	8.181e-5	-15.24
50	7.854e-5	-15.26
49	8.014e-5	-15.25
47	8.355e-5	-15.59
49	8.014e-5	-15.25
		Avg = -15.25, s = 0.0114

Series 2

44		-15.25
43		-15.24
42 (3 reps)	9.133e-5	-15.25
	9.350e-5	-15.23
		Avg = -15.24, s = 0.0089

Series 3

44	8.925e-5	-15.20
46	8.537e-5	-15.22
48 (2 reps)		-15.24
47		-15.23
		Avg = -15.23, s = 0.017

Series 4

41 (3 reps)	9.578e-5	-15.25
39	1.007e-4	-15.23
40	9.817e-5	-15.24
		Avg = -15.24, s = 0.0089

Overall average permeability = -15.238
Overall average standard deviation = 0.0136

The standard deviation in the ASTM D1434 permeability test was reduced by a factor of 11.5 by removing the water bath.

Round-robin Interim Results

The round-robin effort has completed the first nine specimens. Five remain to be analyzed. The results are presented here.

Round-robin Permeability Testing Preliminary Results

Serial Number (S/N)	MSFC Result	SRI Result	PMI Result
S/N 7 Fwd	-14.40	-13.74	*
S/N 75 Fwd	-17.46	-17.5	*
S/N 75 Aft	-13.87	-13.91	-15.17
S/N 76 Aft	Not Analyzed	-14.84	Not Analyzed
S/N 78 Fwd	-15.02	-15.03	-15.38
S/N 95 Fwd	-14.12	-14.15	-15.68
S/N 112 Aft	-15.69	-15.57	*
S/N 113 Aft	-17.32	-17.20	-17.35
S/N 114 Fwd	-16.78	-16.53	-15.34
S/N 115 Aft	-16.61	-16.50	-15.67
S/N 118 Aft	-15.97	-15.94	-15.65
S/N 120 Aft	-15.27	-14.98	-16.04
S/N 121 Fwd	-15.67	-15.94	-15.47
Graphite Phenolic	-10.83	-------	*
2219 Aluminum	-20.69	-------	*

S/N 76 AEC Aft tag end was not analyzed by MSFC due to it being a unique size requiring a special holding fixture. S/N's 7 Fwd, 75 Fwd, 75 Fwd, and 112 Aft were not analyzed by PMI because they are in the second part of the round-robin where PMI will generate statistical data on their test method.

Found Robin Permeabilit, Test Results

SRI, MSFC, and PMI Test Results

Summary of the Round-Robin Specimen Results
MSFC ASTM D1434 Test

Specimen	SRI Permeability	MSFC Values				Number of Replicates
		High	Low	Ave	Std Dev	
Graphite Phenolic	------	-11.20	-10.46	-10.83	0.4102	6
S/N 7 Fwd	-13.74	-14.42	-14.36	-14.40	0.0260	12
S/N 75 Aft	-13.91	-13.90	-13.85	-13.87	0.0213	15
S/N 75 Fwd	-17.5	-17.50	-17.40	-17.46	0.0420	4
S/N 78 Fwd	-15.03	-15.03	-14.98	-15.02	0.0136	20
S/N 95 Fwd	-14.15	-14.15	-14.10	-14.12	0.0216	6
S/N 112 Aft	-15.57	-15.73	-15.64	-15.69	0.0374	6
S/N 113 Aft	-17.20	-17.46	-17.18	-17.32	0.1980	2
S/N 114 Fwd	-16.53	-16.83	-16.72	-16.78	0.0445	5
S/N 115 Aft	-16.50	-17.39	-15.78	-16.61	0.841	6
S/N 118 Aft	-15.94	-16.07	-15.80	-15.97	0.1264	5
S/N 120 Aft	-14.98	-15.32	-15.15	-15.27	0.0727	6
S/N 121 Fwd	-15.94	-15.75	-15.61	-15.67	0.0591	6
2219 Aluminum	------	-21.08	-20.23	-20.69	0.4178	4

Figure 8

Round Robin Permeabilit, Prelim Results

Raw Data, Individual Values

Specimen

Round Robin Permeability, Prelim Results

Raw Data, Individual Values

Specimen
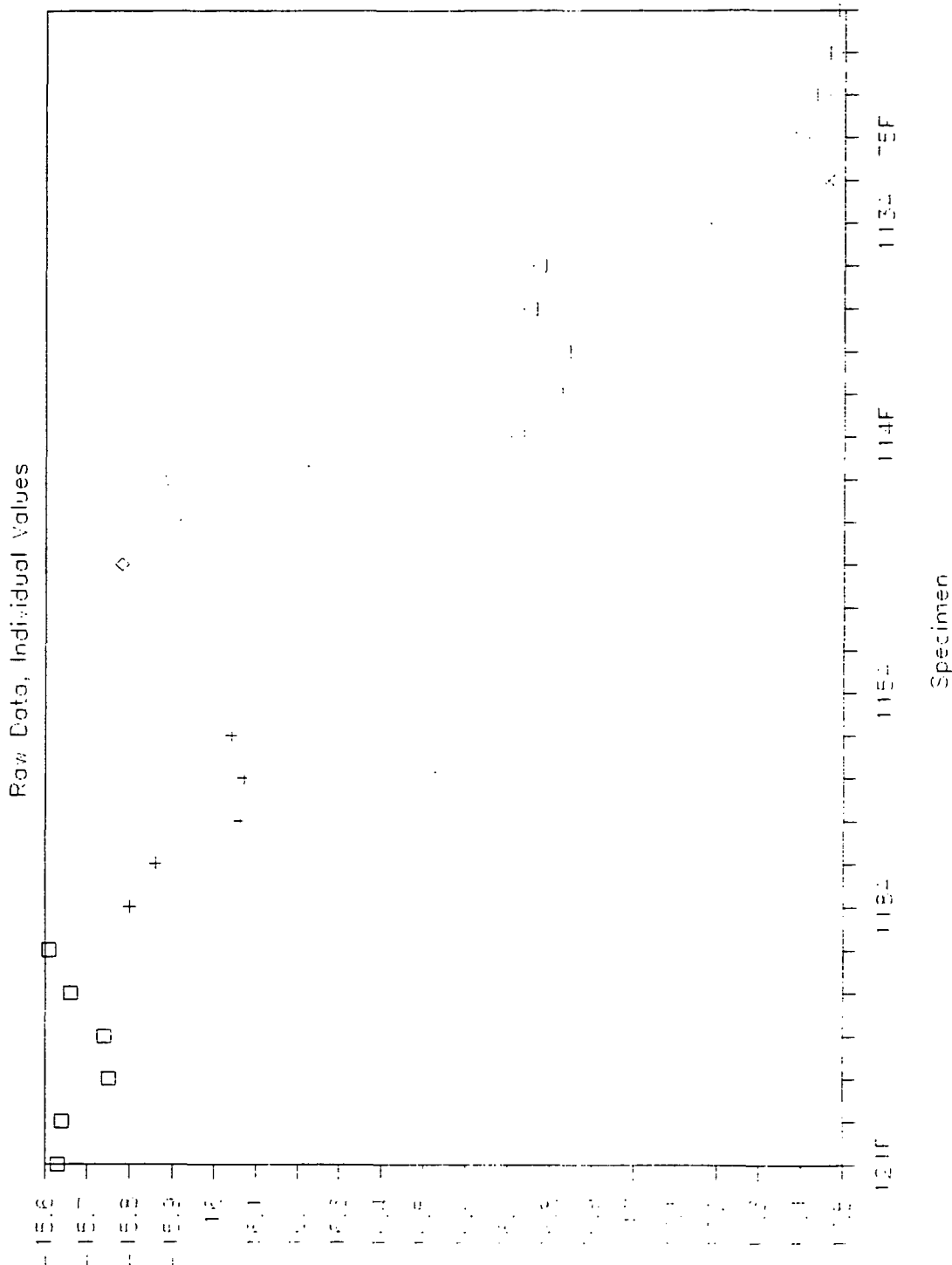
Remaining to be effected on the test are:

1. Capillary tubes that do not require shimming to avoid leaks. These tubes are on order.

2. A pressure gage that will allow the use of up to 180 psig permeating gas. This will speed the testing further and allow specimens of lower permeability to be analyzed.

3. Temperature Control of the Lab or better insulation around the permeability test apparatus to maintain isothermal conditions.

4. Development of the Forcheimer equation to determine when permeability test results are outside the assumptions of the Darcy equation. This will be placed into the current computer program used to calculate Darcy constants.

The Permeability Equation
(See *Chemical Engineers' Handbook*, 5th Ed., page 5-54)

For an Isothermal Ideal Gas:

$$(P_1^2 - P_2^2) / L = (2\alpha RT\mu G) / (M g) + (\beta + (1/L)\ln(P_1/P_2)) + (2RTG^2)/M g$$

Where:

P_1 = Absolute Upstream Pressure
P_2 = Absolute Downstream Pressure
L = Specimen Thickness
R = Gas Constant
T = Absolute Temperature
μ = Permeating Gas Viscosity
G = Mass Velocity of the Gas
M = Molecular Weight of the Gas
g = Gravitational Dimensional Constant
α = viscous resistance coefficient, the inverse of The Darcy Constant
β = inertial resistance coefficient

For purely viscous flow, the far right term is negligible. G is usually expressed in volumetric units, and the equation becomes

$$1/\alpha = B = (2RT\mu dQL) / (AM (P_1^2 - P_2^2))$$

Where:

B = The Darcy Constant
Q = Permeating Gas Volumetric Flow Rate
d = Density of the Permeating Gas
A = Area of the specimen the Permeating Gas Flows through

Permeability Measurement Observations

1. Carbon Phenolic Specimens of relatively low permeability are associated with observed "pulsations" (temporary capillary plug arrest). This is not observed in specimens of relatively high permeability.

   Possible explanation – formation of "bubbles" due to the labile chemical mixture of solvent, water, oligimers, etc., in cured phenolic interacting with the surface of the few pores available for flow. A dynamic process similar to the PMI bubble point test?

2. Specimen handling effects.

   PMI RGA Permeability Results
   S/N 75 AEC   -15.17

   After a weekend in a vacuum desiccator
   S/N 75 AEC   -15.85

   SRI Handling

   S/N 7 and 113 AEC were polished on one surface using 600 grit sandpaper. SRI estimates that this will increase measured permeabilities. This was observed.

Permeability Results	SRI	MSFC
S/N 7 AEC	-13.74	-14.40
S/N 113 AEC	-17.20	-17.32

PAT PINOLI

RSRM/SPIP CARBON PHENOLIC MATERIAL

PERFORMANCE TQM TEAM ACTIVITY

Karl Fischer Analysis of Moisture Effusion

Presented to the
12th Biannual IAC Meeting
Mississippi State University
Starkville, Mississippi
May 18, 1994

Pat C. Pinoli
Lockheed R&DD

Summary of LPARL Test Procedure

1. Dry cut 7 mm^3 test specimens

   - ±0.5 mm

   - Fabric plane orientation

2. Obtain initial specimen weight ±0.1 mg

3. Introduce specimen into R.T. quartz boat

4. Start run - automatic insertion into isothermal oven (e.g., 500°F)

5. Data acquisition is limited to 120 moisture effusion data points - options A or B

   A. 1 minute intervals, up to 2 hours

   B. 15 second intervals, up to 30 minutes

Summary of LPARL Test Procedure

6. Data plot options

   A. Moisture effusion rate vs. time

   B. Cumulative moisture effusion vs. time

      - Time dependent average rate

7. Specimen is retracted and allowed to cool to RT after isothermal exposure

8. Specimen is removed and weighed to nearest 0.1 mg

9. Total weight loss and total moisture effusion wt % values are calculated

10. Percent moisture in total weight loss calculated

OBJECTIVE

- Assess the potential of Karl Fischer analysis to provide performance related data

  - Total residual volatiles @ 325 & 500°F

  - Total moisture effusion @ 325 & 500°F

  - Ratio of moisture to total volatile effusion

  - Moisture effusion differential rate vs. time plot

  - Cumulative moisture effusion vs. time plot

  - Initial moisture effusion acceleration rate

Karl Fischer Apparatus Flow Diagram

CARRIER GAS OUT

TO TITRATION CELL

PURGED GAS
DISCHARGE VALVE

FLOWMETER

FLOW CONTROL VALVE

CARRIER
GAS IN

HEATER

ZEOLITE CONTAINER

SILICA GEL CONTAINER
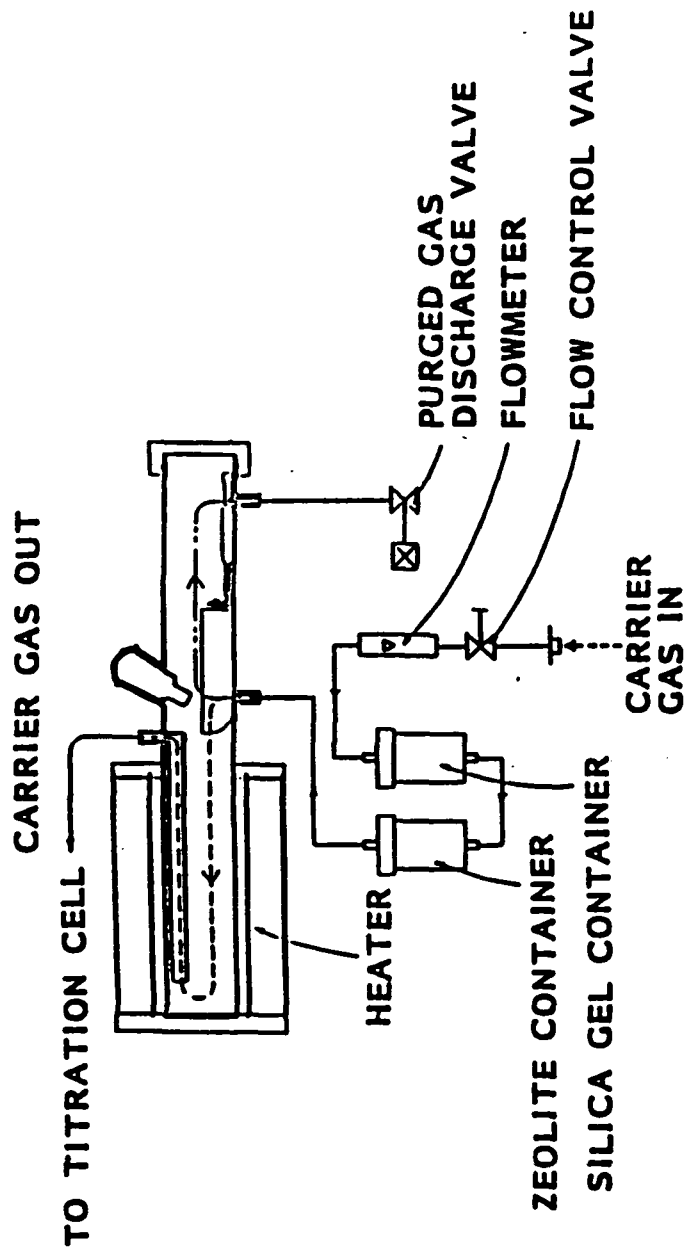
——— BACK-PURGING (PURGED GAS DISCHARGE VALVE: OPEN)

- - - - - CELL PURGING (PURGED GAS DISCHARGE VALVE: CLOSED)

IMPROVED ABLATIVE MATERIAL PROGRAM

Karl Fischer Data Summary

Preliminary
2 hours at 500°F, Inert Gas, $7 \times 7 \times 7 \text{ mm}^3$

RSRM Reference	Total Water w%	Total Volatiles w%	% Water in Volatile Gas
AEC FSM-1-2 Fwd Tag End	3.63	4.35	83.4
AEC 17A Aft End	2.42	2.66	91.0
4 hr run	3.00	3.31	90.6
AEC 3A	4.61	4.87	94.7
AEC 2A Fwd End	4.28	4.48	95.5
AEC TEM-7-1 Fwd Tag End	3.59	3.97	90.4
2nd 2 hours	0.25	0.52	48.1
Total	3.84	4.49	85.5

IMPROVED ABLATIVE MATERIAL PROGRAM

Karl Fischer Data Summary

Preliminary
2 hours at 500°F, Inert Gas, 7 x 7 x 7 mm^3

RSRM Reference	Total Water w-%	Total Volatiles w-%	% Water in Volatile Gas
Cowl 17A	3.58	4.00	89.5
HDHU-1 (NAR) Baseline	3.30	3.76	87.8
2nd 2 hours	0.36	0.47	77.0
Total	3.66	4.23	86.5
AEC S/N 12 (Avtex)	3.88	4.11	94.4
Avtex Baseline 315-Oring 504 (6071)	4.10	4.52	90.7
23-HRPU-1	3.71	4.11	90.3
HRHU Billet	3.26	3.88	84.0
23-HRPF	3.51	3.95	88.9

ASRM

IMPROVED ABLATIVE MATERIAL PROGRAM

Karl Fischer Analysis of Water Loss at 500°F

IMPROVED ABLATIVE MATERIAL PROGRAM

Karl Fischer Analysis of Water Loss at 500°F

Rate of Water Desorbed (mg/min/gram) vs **Desorption Time (minutes)**

LEGEND

O 315 O-ring 504(6071), Avtex Baseline

KARL FISCHER ANALYSIS

Karl Fischer Analysis of Water Loss at 500°F

ASRM
IMPROVED ABLATIVE MATERIAL PROGRAM

Karl Fischer Analysis of Water Loss at 500°F
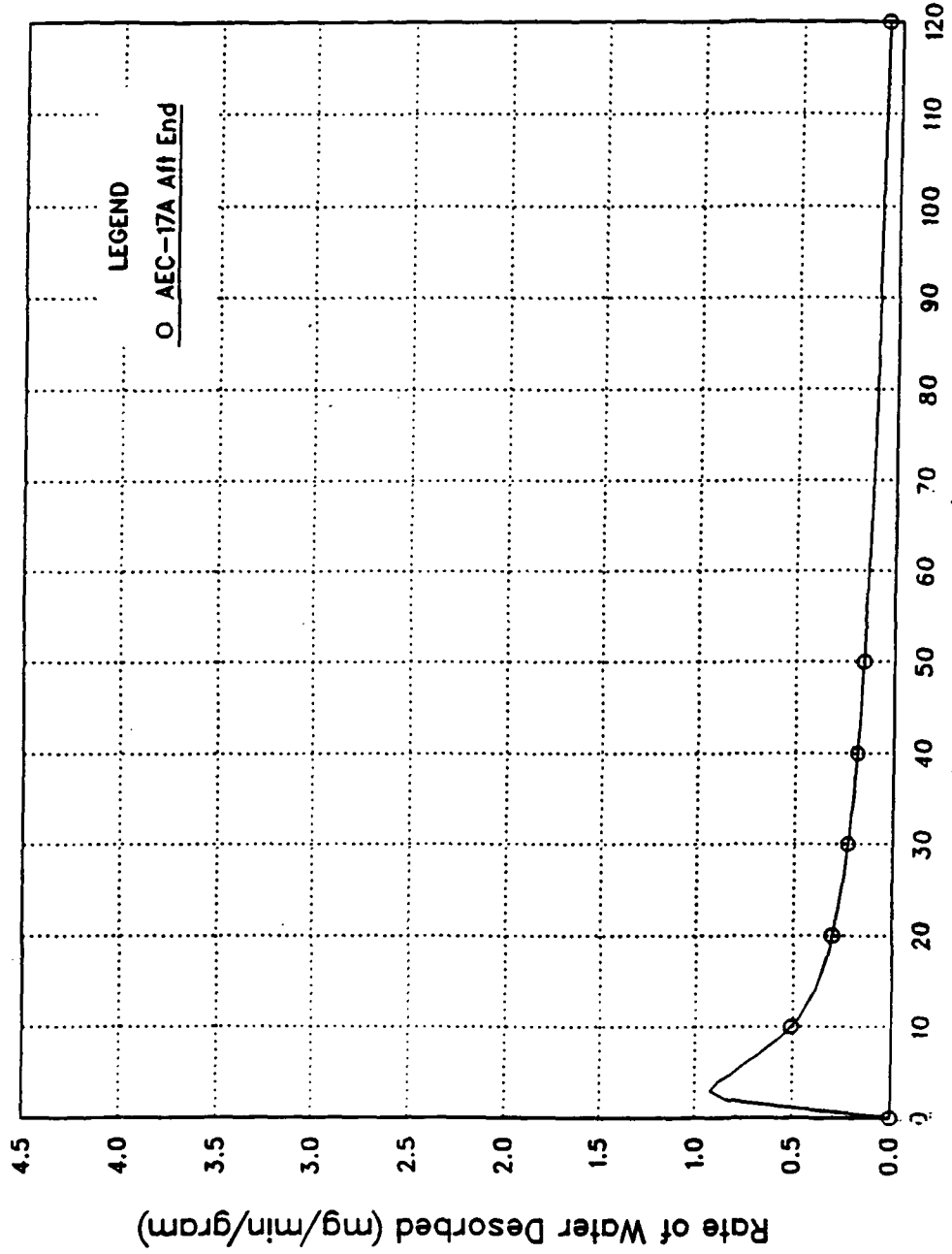
TEMPERATURE RISE
ADP-351 EVAPORATOR (KARL FISCHER ACCESSORY APPARATUS)
Standard Density Carbon Phenolic (HDHU)

LEGEND
500°F (3)
500°F (1)
325°F (4)
325°F (3)

Karl Fischer Analysis of Water Loss at 500°F
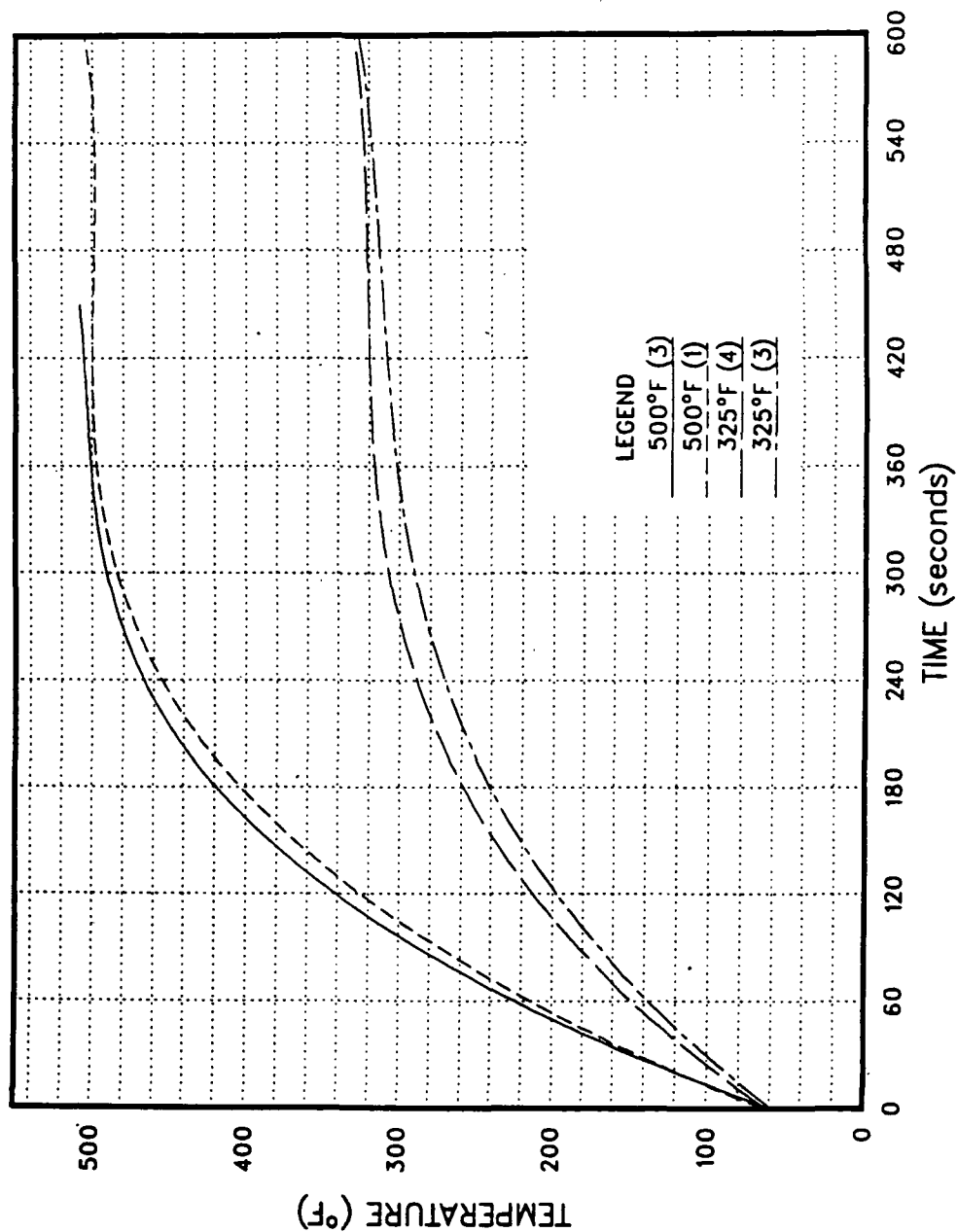
KARL FISCHER ANALYSIS
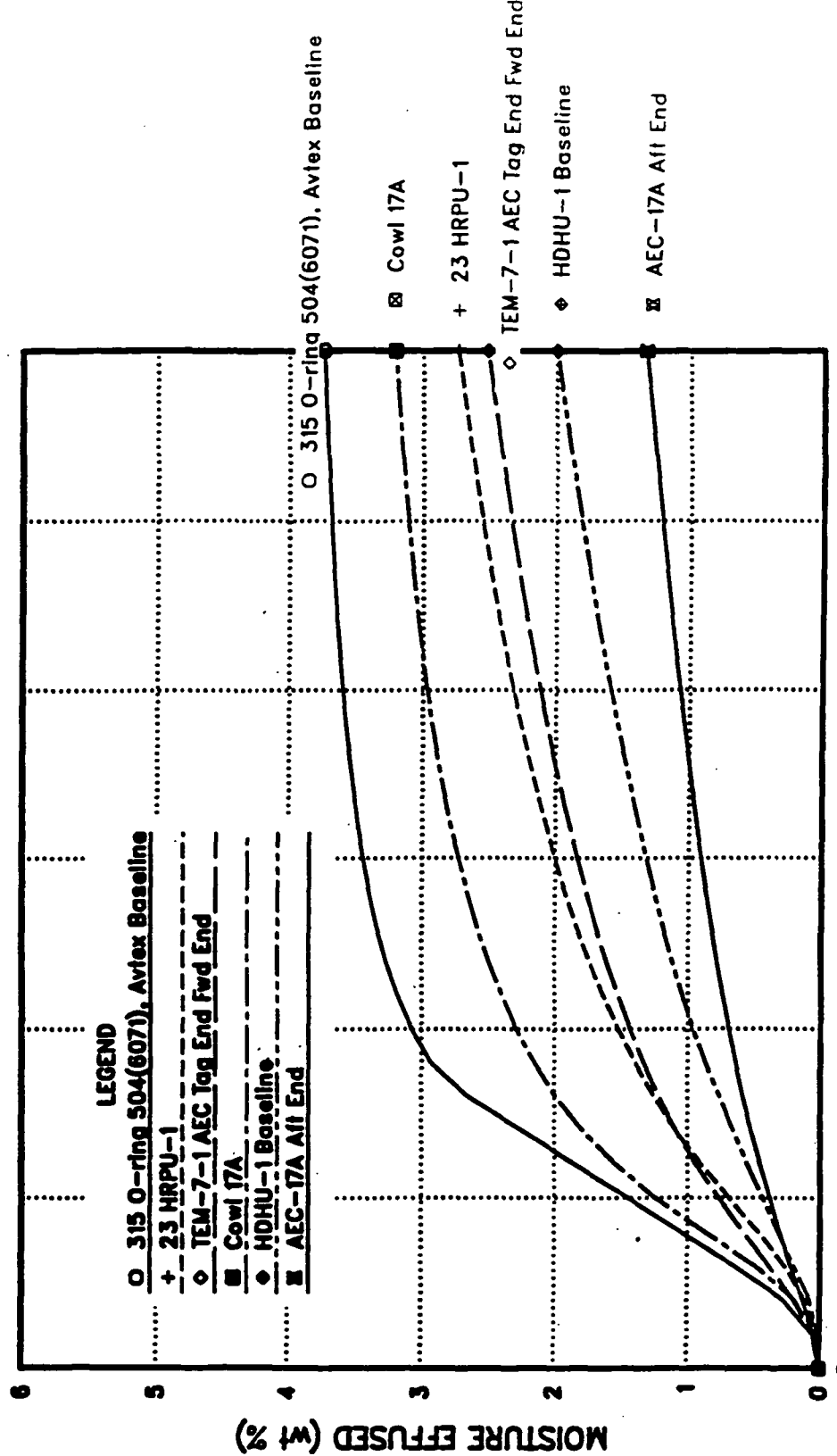
TESTING DATA GENERATION

- Total residual volatiles effusion @ 500°F

- Total moisture effusion @ 500°F

- Ratio of moisture to total volatiles effusion

- Moisture effusion differential rate vs. time plot

- Cumulative moisture effusion vs. time plot

- Initial moisture effusion acceleration rate

- Isothermal moisture effusion rate

KARL FISCHER ANALYSIS

GROUND RULES FOR KARL FISCHER TESTING

- Test only fully characterized and identified pedigree material (permeability/mechanicals/fiber precursor/prepreg/etc.)

- All testing to be performed at 500°F

  - Isothermal time of 120 minutes

  - Specimen size of 7 cubic mm

- Moisture effusion measured at 1 minute intervals

- Plot moisture effusion differential rate vs. time

- Plot cumulative moisture effusion vs. time

  - Determine initial effusion rate

PRODUCT OF EFFORT

- Performance related tag end acceptance test for ply-lift
  - Performance related prepreg acceptance test for ply-lift
  - Performance related constituent acceptance test for ply-lift
  - Performance related processing acceptance test for ply-lift
- Fundamental understanding of the ply-lift mechanism
- Provide analytical code verification data

RECOMMENDED APPROACH

- Test tag end material and fired virgin material at 500°F, ply-lift vs. no ply lift (12 x 3 = 36 runs)

- Review ASRM/KF Data Base on Standard Density Material

- Conduct fundamental testing to verify pore pressure phenomenology (500°F)

  - Assess the relationship of round robin permeability data to moisture effusion data

  - Tag end BP vs. ICI behavior

  - Effusion anisotropy (fiber vs. cross ply effusion data)

  - Assess within part variability

  - Effusion relationship to temperature on the same sample. Stepped isothermal runs @ 325, 400, and 500°F

  - Effusion behavior of 325 vs. 500°F

FRANK STONE AND DAVID KINCHEN

STATISTICAL METHODS

MEASUREMENT

IS A

PROCESS

STATISTICAL METHODS

STATISTICAL METHODS

INTRACLASS CORRELATION

r = 0.944

μ = 114.52 (+)

$$D_R = \sqrt{\frac{1+r}{1-r}} = 5.89$$
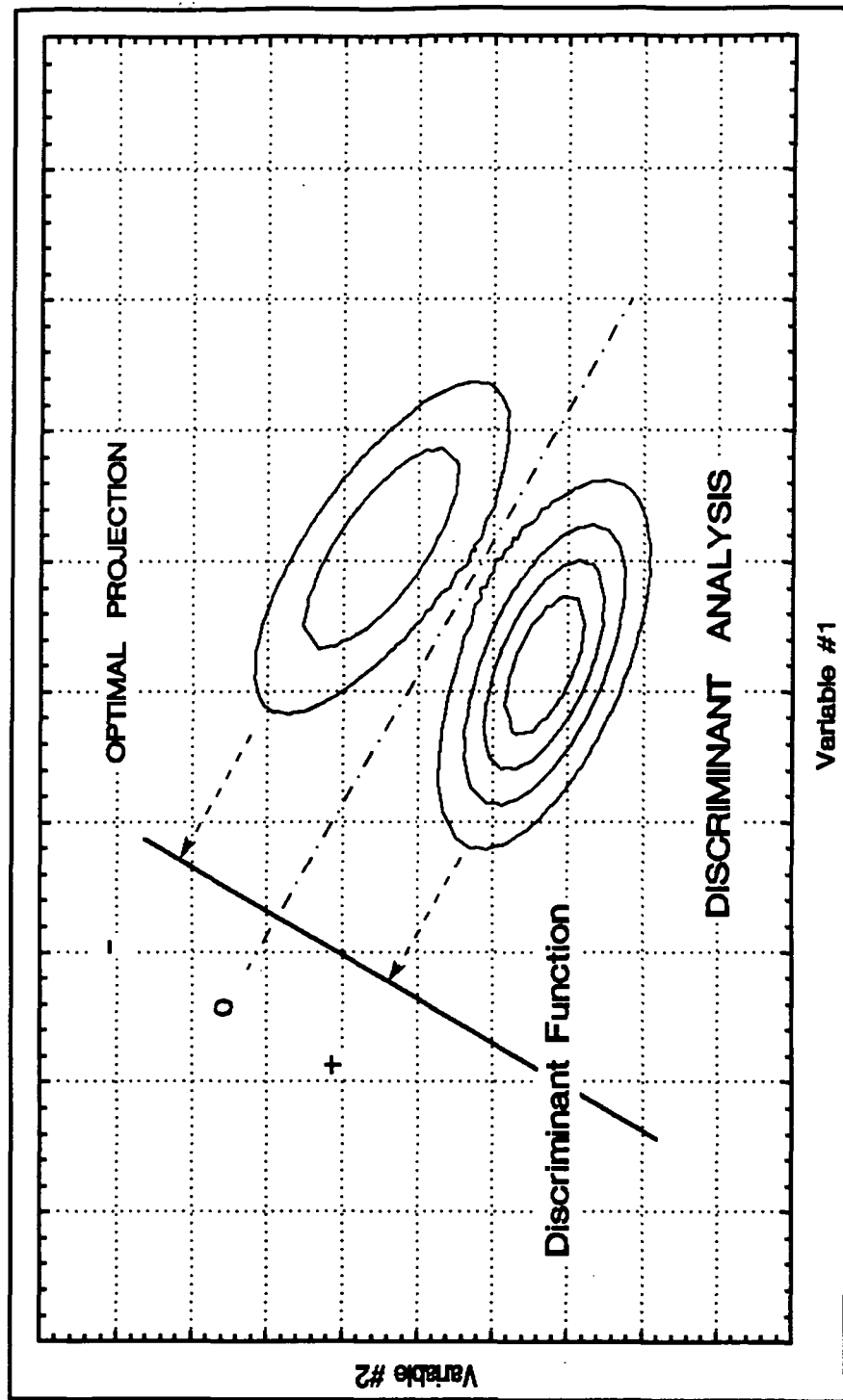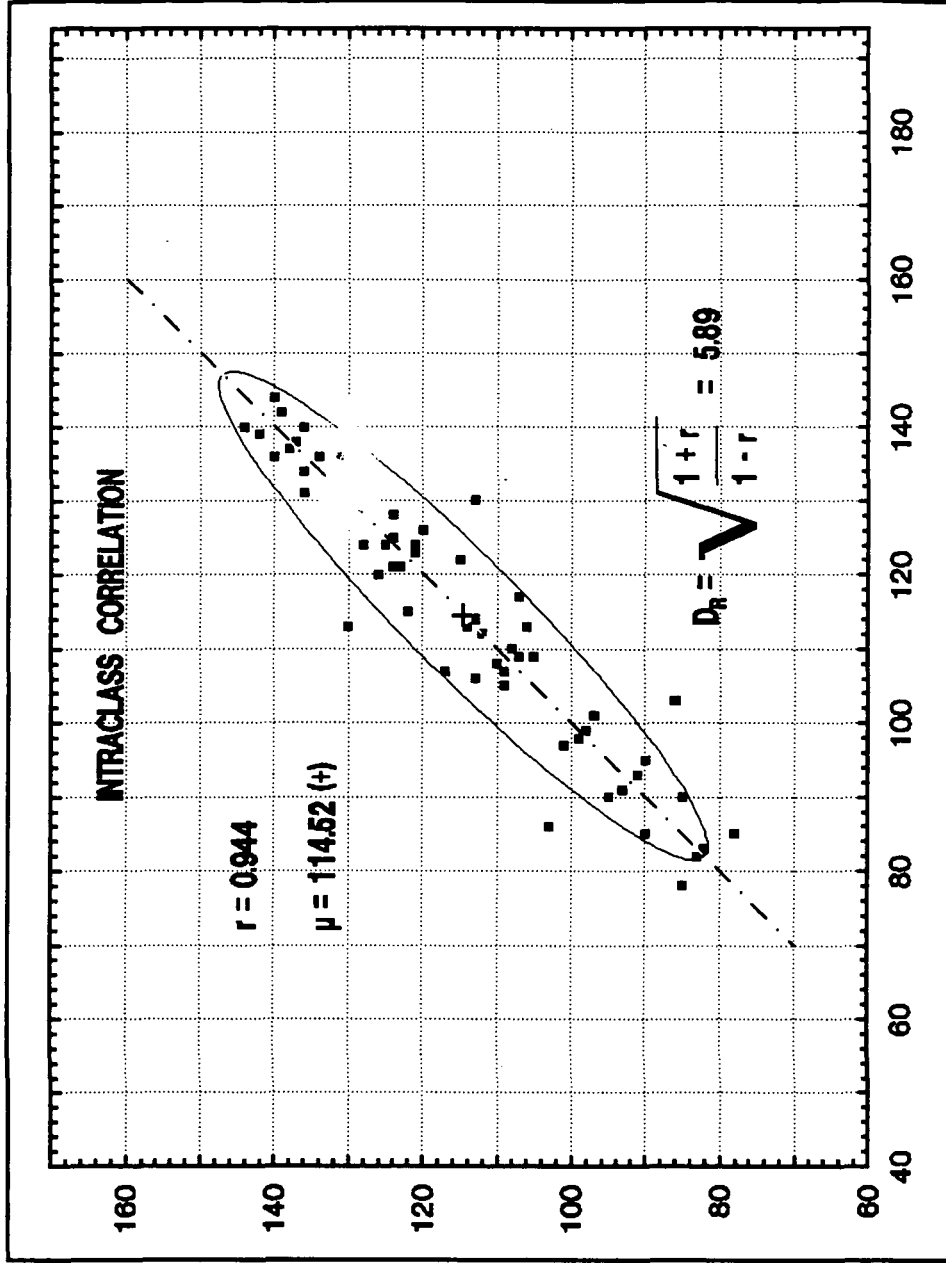
STATISTICAL METHODS
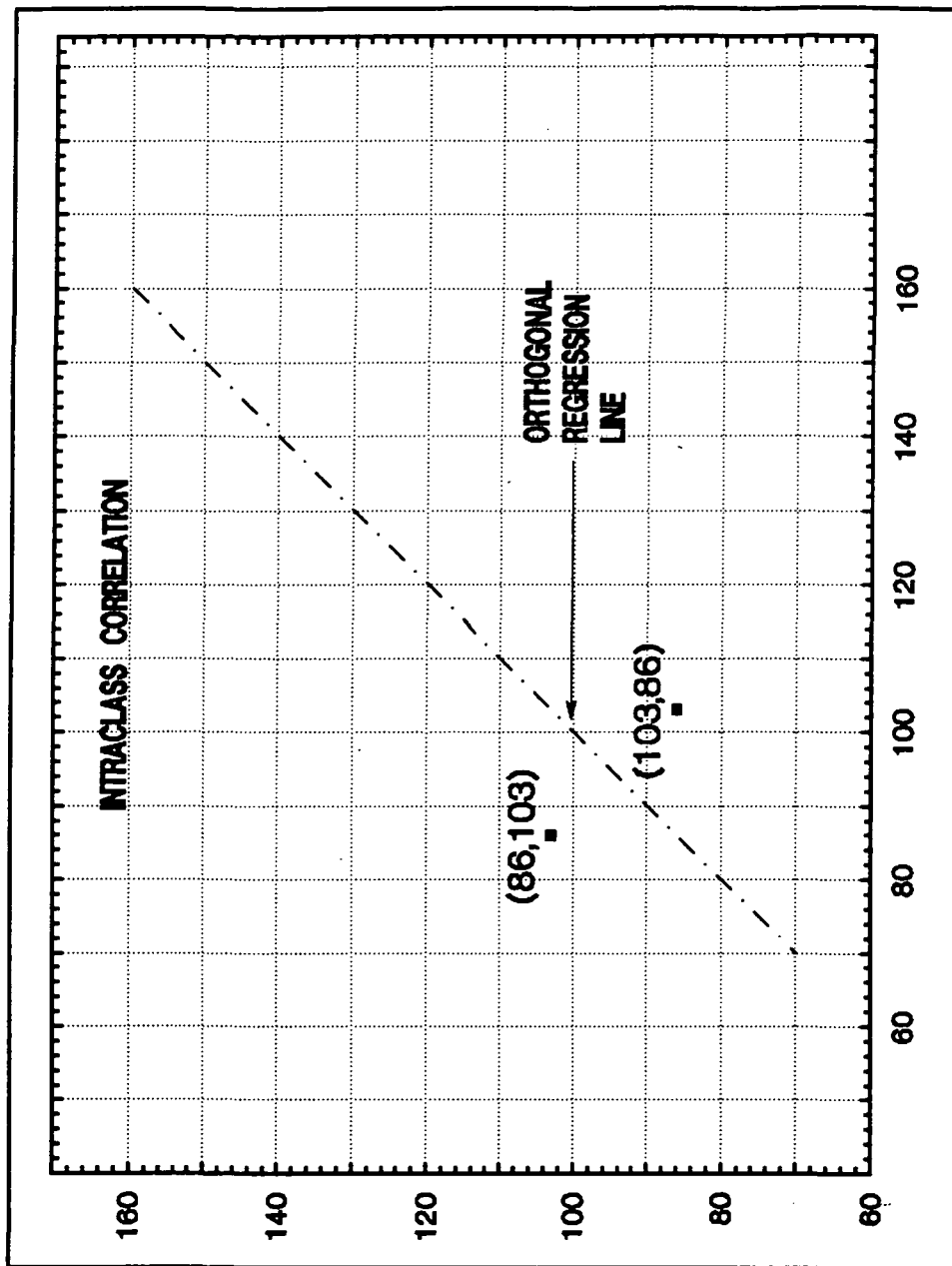
STATISTICAL METHODS

PURPOSE OF MEASUREMENT

To Provide A Meaningful Level of Discrimination ---

Go/NoGo
Pass/Fail
Color
Rank
Weight
Dimensions

Specifically: 1. Do the raw materials conform to requirements?
2. Will the end product perform to requirements?

STATISTICAL METHODS

UNITS OF MEASURE

MUST BE ADEQUATE TO DISCRIMINATE PRODUCT

Qualitative vs. Quantitative

STATISTICAL METHODS

DEFINITIONS OF MEASUREMENT

1. The act or process of measuring,
2. A figure, extent, or amount obtained by measuring.

MEASURE

1. A portion,
2. A moderate degree,
3. A group of musical beats,
4. A basis of standard or comparison.

Source: Webster,s Dictionary

STATISTICAL METHODS

No two things are alike, but even if they were,
we would still get different values when we measure them.

SOURCES OF VARIATION IN MEASUREMENT

VALUABLE

Lot -- Lot
Part -- Part

VALUELESS

Laboratory -- Laboratory
Machine -- Machine
Operator -- Operator
Time -- Time
Method -- Method

STATISTICAL METHODS

Repeatability & Reproducibility Summary Plot

No. of Operators: 3 (variable: TOOL)
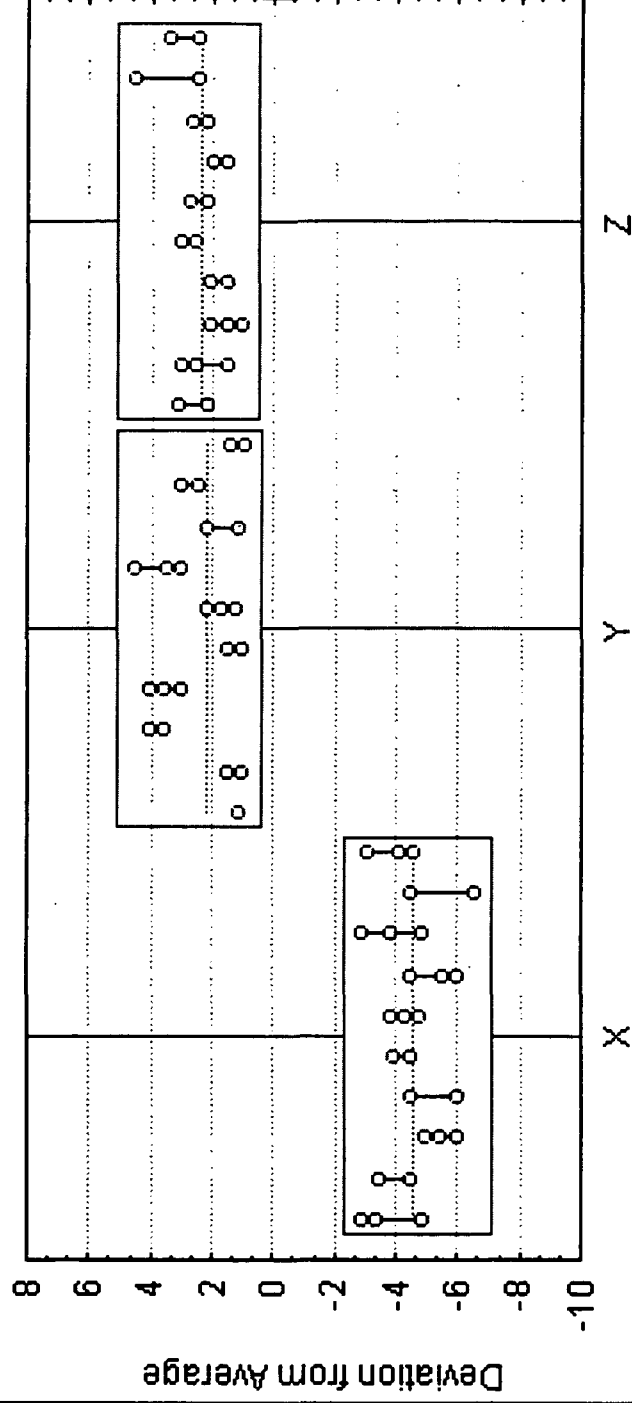
No. of Parts: 10 (variable: PART)

No. of Trials: 3 (variable: OPER)

STATISTICAL METHODS

Plot of Average Measurements by Tool and Part

No. of Operators: 3 (variable: TOOL)

No. of Parts: 10 (variable: PART)

No. of Trials: 3 (variable: OPER)
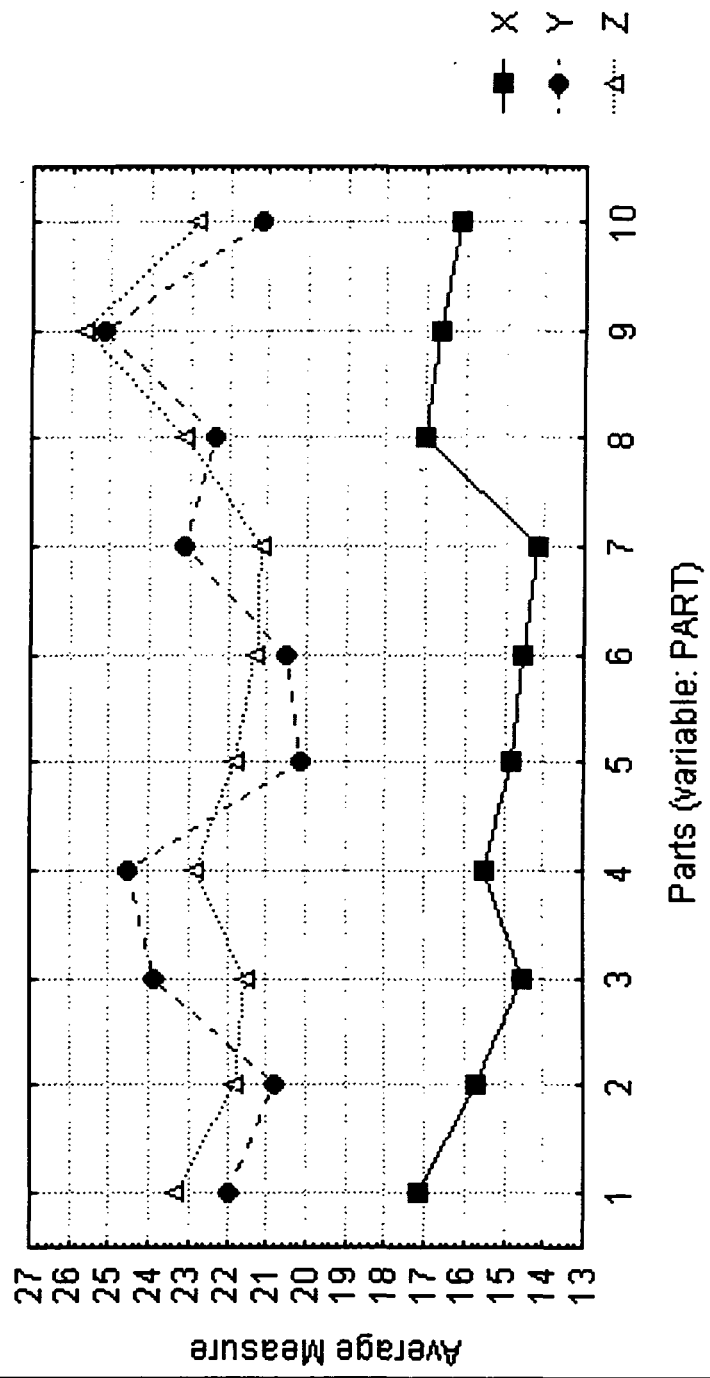
STATISTICAL METHODS

CONSISTENCY

Relative Characterisic

Compares REPEATED Measures of the same item over TIME.

Impacted by VALUELESS components:

STATISTICAL METHODS

BIAS

Relative Characteristic

Compares Mesurement Results to a Known/Accepted Reference

Impacted by VALUELESS components:
Operators, Machines, Shifts, Labs

STATISTICAL METHODS

BASIS OF MEASUREMENT METHOD

Procedure

Unit of Measure

Consistency

Bias

STATISTICAL METHODS

PROCEDURE

Written, Clear, Consise, Unambiguous

Descriptive and Perscriptive

Details Steps and Sequence

Materials Storage, Handling and Conditioning

Setup, Calibration, Verification, Replication

Calculations, Reporting Format

Familiarity With Procedure(Certification)

STATISTICAL METHODS
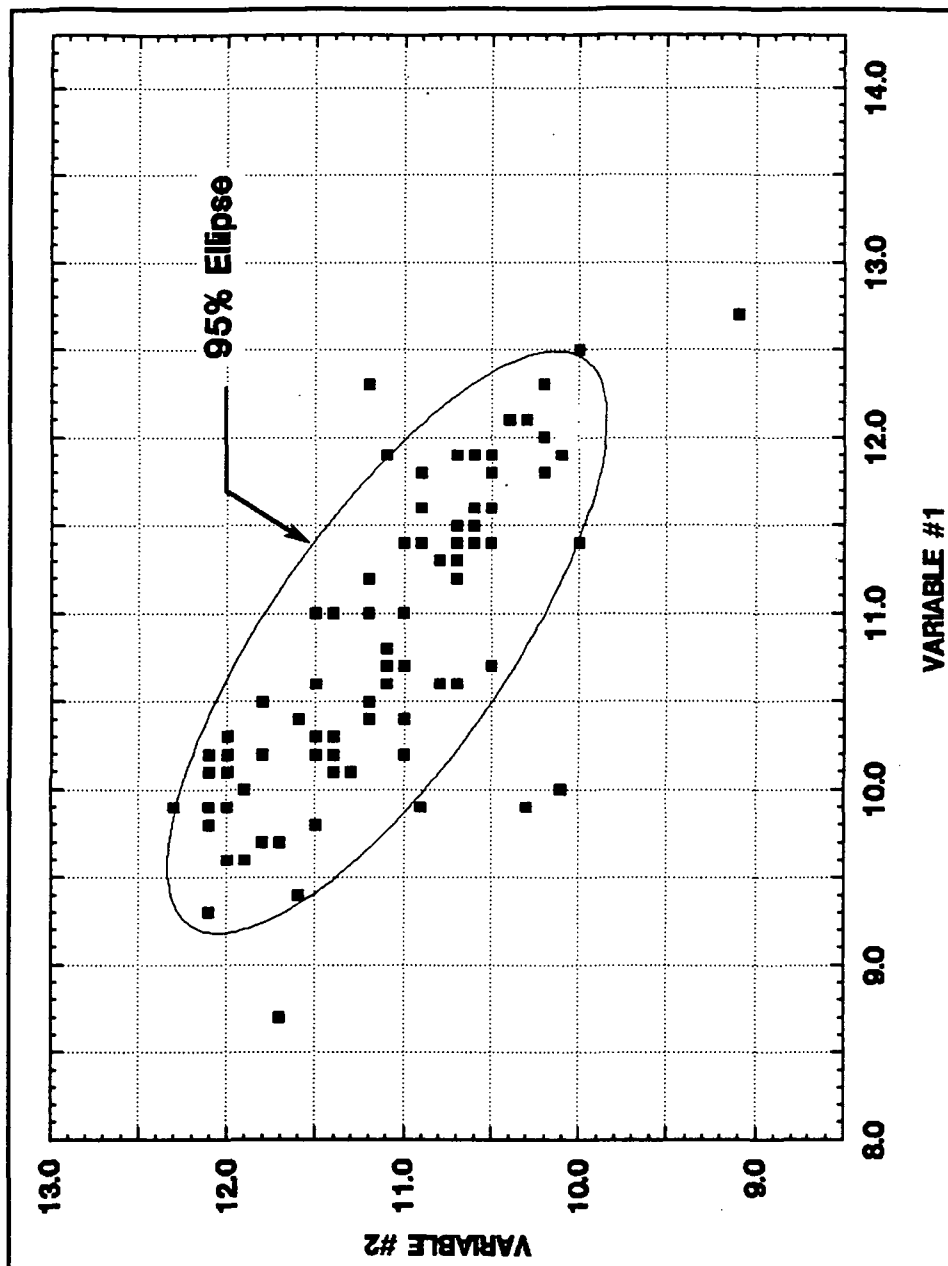
STATISTICAL METHODS

From: Analysis of Variance (egapemp.css)

Variable: MEASURE
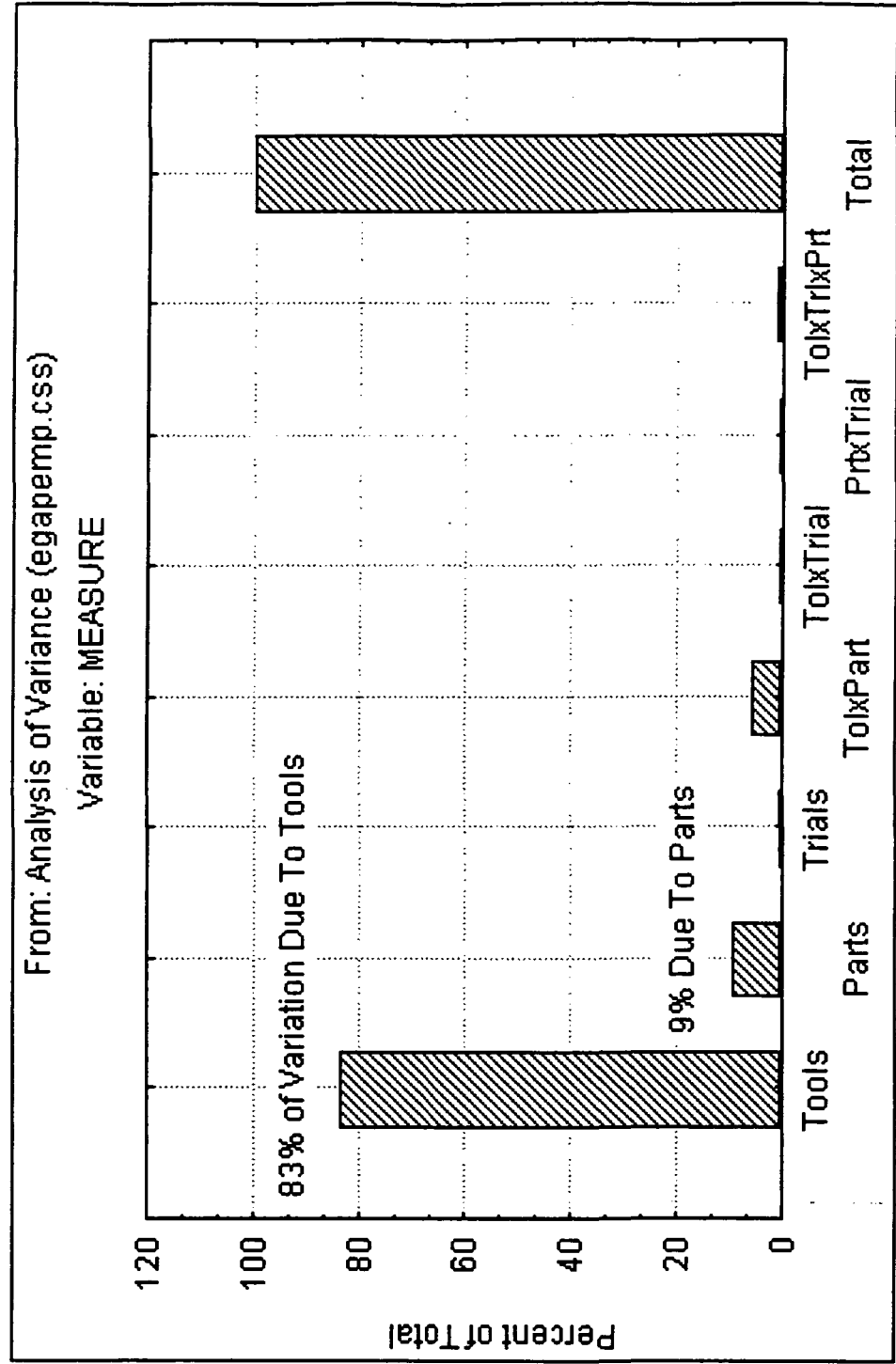
STATISTICAL METHODS

ROUND ROBIN TESTING

Master Table

Summary of Design for R & R Study

Laboratories: 5   Samples: 12   Trials: 3

Run Number	Lab Number	Sample I.D.	Trial Number	Meas. Result
1	1	1	1	
2	1	2	1	
3	1	3	1	
4	1	4	1	
5	1	5	1	
6	1	6	1	
7	1	7	1	
8	1	8	1	
9	1	9	1	
10	1	10	1	
11	1	11	1	
12	1	12	1	
13	1	1	2	
14	1	2	2	
15	1	3	2	
16	1	4	2	
•	•	•	•	
•	•	•	•	
•	•	•	•	
180	5	12	3	

STATISTICAL METHODS

DISCRIMINANT ANALYSIS

VARIABLE #1

VARIABLE #2

STATISTICAL METHODS

PERMEABILITY TESTING

Round Robin Results

SAMPLES (14)

7F	114F
75A	115A
75F	118A
78F	120A
95F	121F
112A	Graphite Phenolic
113A	2219 Al Disk

STATISTICAL METHODS

Interlaboratory Study
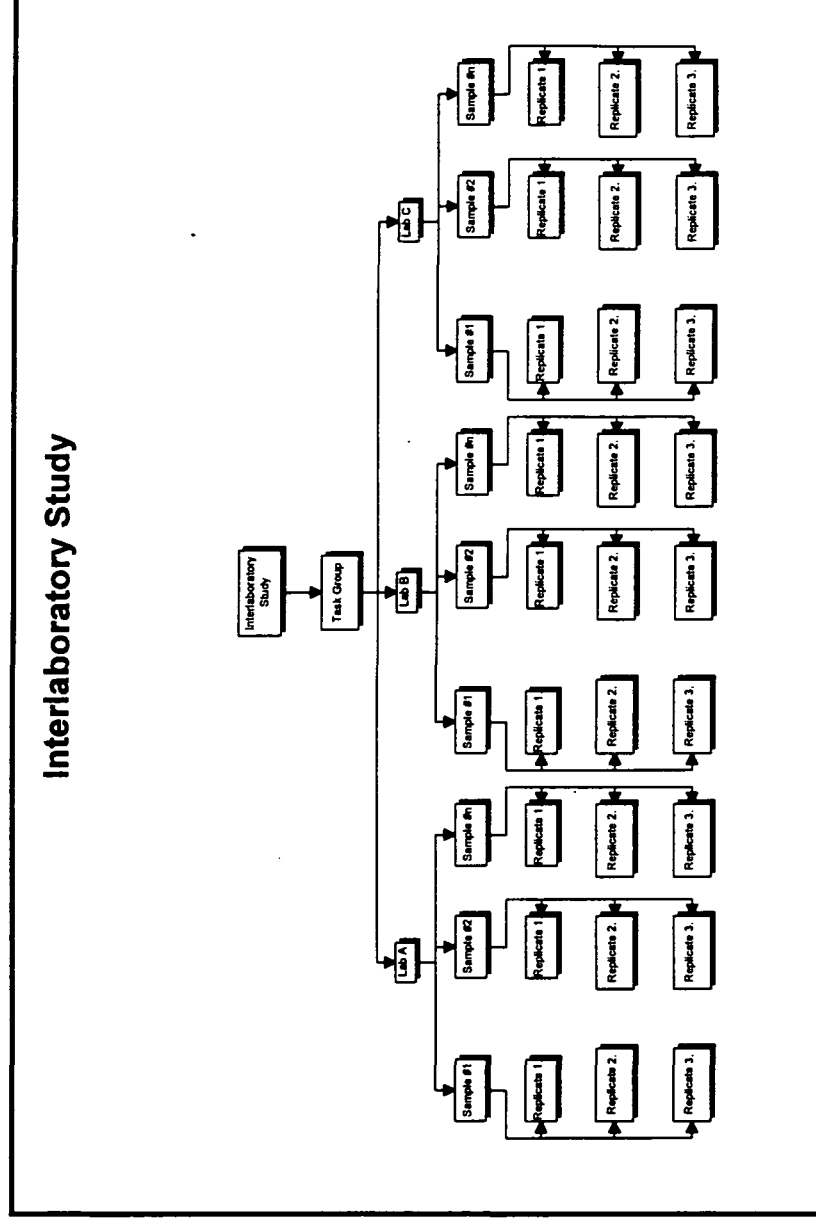
STATISTICAL METHODS

PERMEABILITY TESTING

Round Robin Results

Descriptive Statistics
(Sample Averages - Darcy)

Lab	No.	Min.	Max.	Mean	Std. Dev.
MSFC	12	-17.46	-13..	-15.68	1.204
SRI	12	-17.50	-13.74	-15.58	1.250
PMI	9	-17.20	-15.24	-15.75	0.601

STATISTICAL METHODS

PERMEABILITY TESTING

Round Robin Results

Testing Activity

Laboratory	Samples	Measurements
MSFC	14	103
SRI	12	12
PMI	9	12

STATISTICAL METHODS
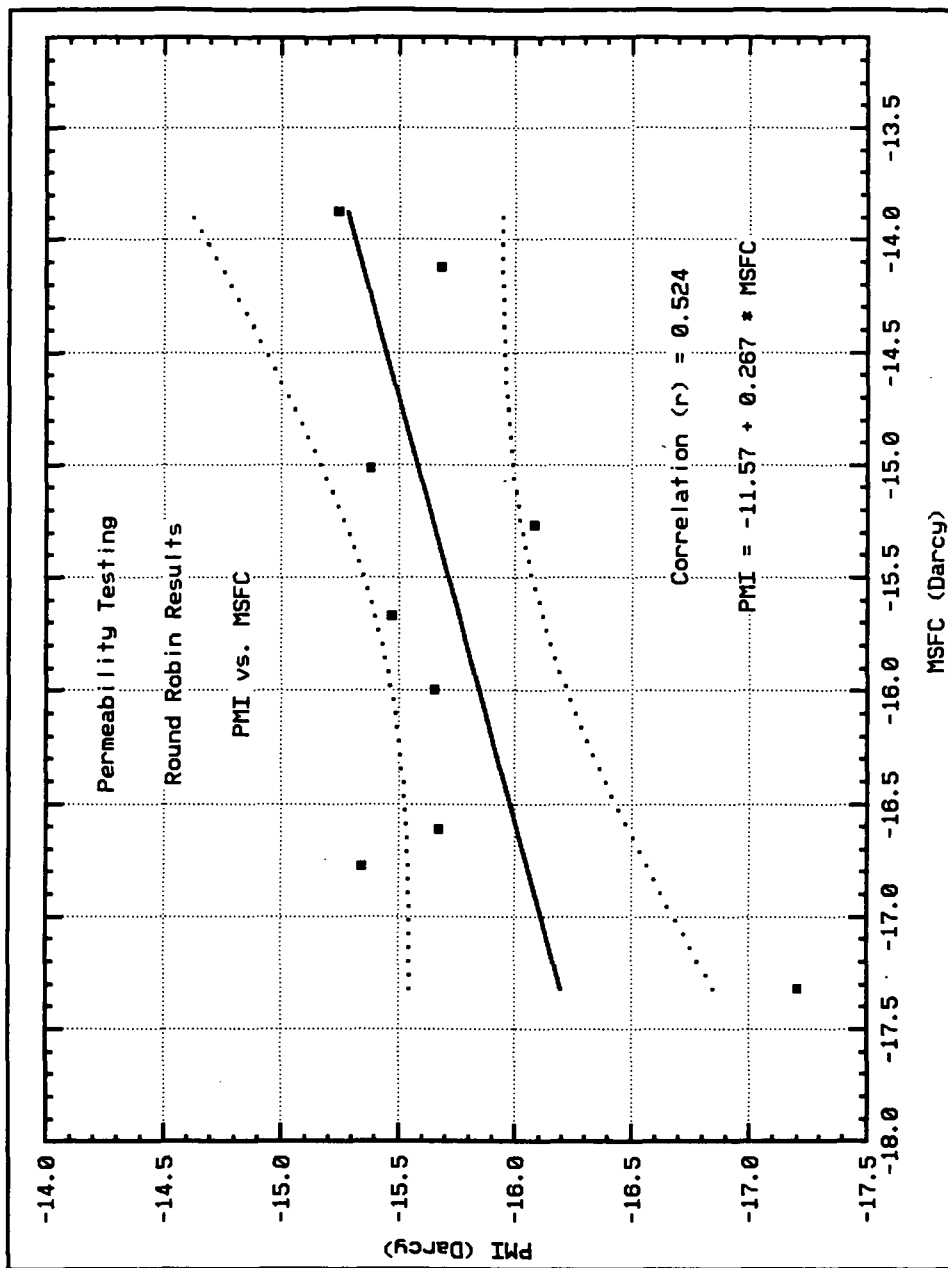
Permeability Testing

Round Robin Results

PMI vs. MSFC

Correlation (r) = 0.524

PMI = -11.57 + 0.267 * MSFC

MSFC (Darcy)

PMI (Darcy)

STATISTICAL METHODS

Permeability Testing

Round Robin Results

SRI vs. MSFC

Correlation (r) = 0.983

SRI = 0.428 + 1.021 * MSFC

MSFC (Darcy)

SRI (Darcy)
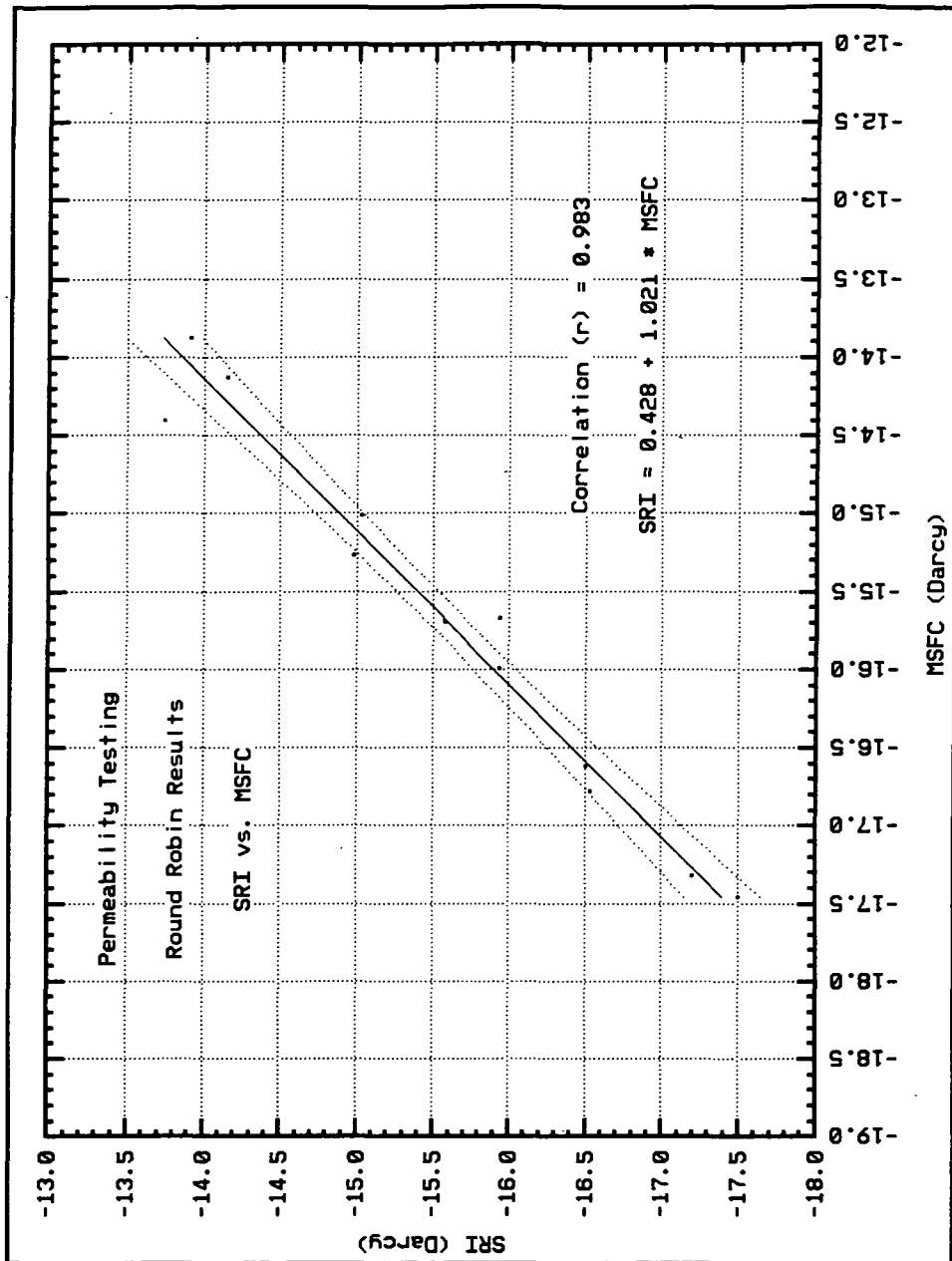
STATISTICAL METHODS

PERMEABILITY TESTING

Round Robin Results

Measurement Uncertainty (95%)

Lab	Measurements	95% Limit
MSFC	206	± 0.150 Darcy
SRI	9	± 0.053 Darcy

STATISTICAL METHODS

Permeability Testing

Round Robin Results

PMI vs. SRI

Correlation (r) = 0.502

PMI = -11.57 + 0.268 * SRI

STATISTICAL METHODS

Permeability Testing

Round Robin Results

Interclass Correlation

MSFC Data

Exploded View

"X" (Darcy)

"Y" (Darcy)

-14.0   -14.5

-14.5   -14.0

STATISTICAL METHODS

Permeability Testing

Round Robin Results

Interclass Correlation

MSFC Data

206 Values

Correlation (r) = 0.994

Discrimination Ratio (D_r) = 18.27
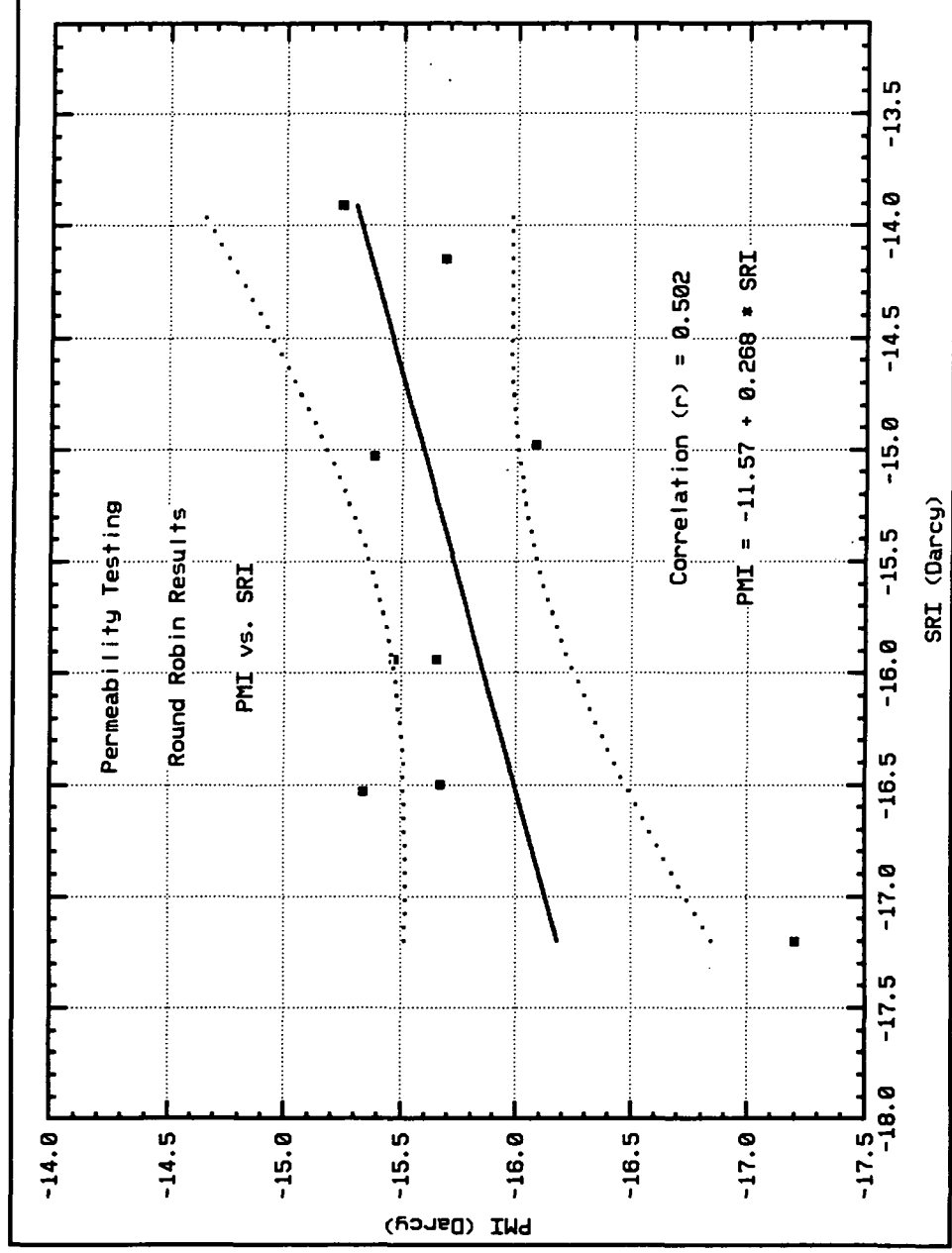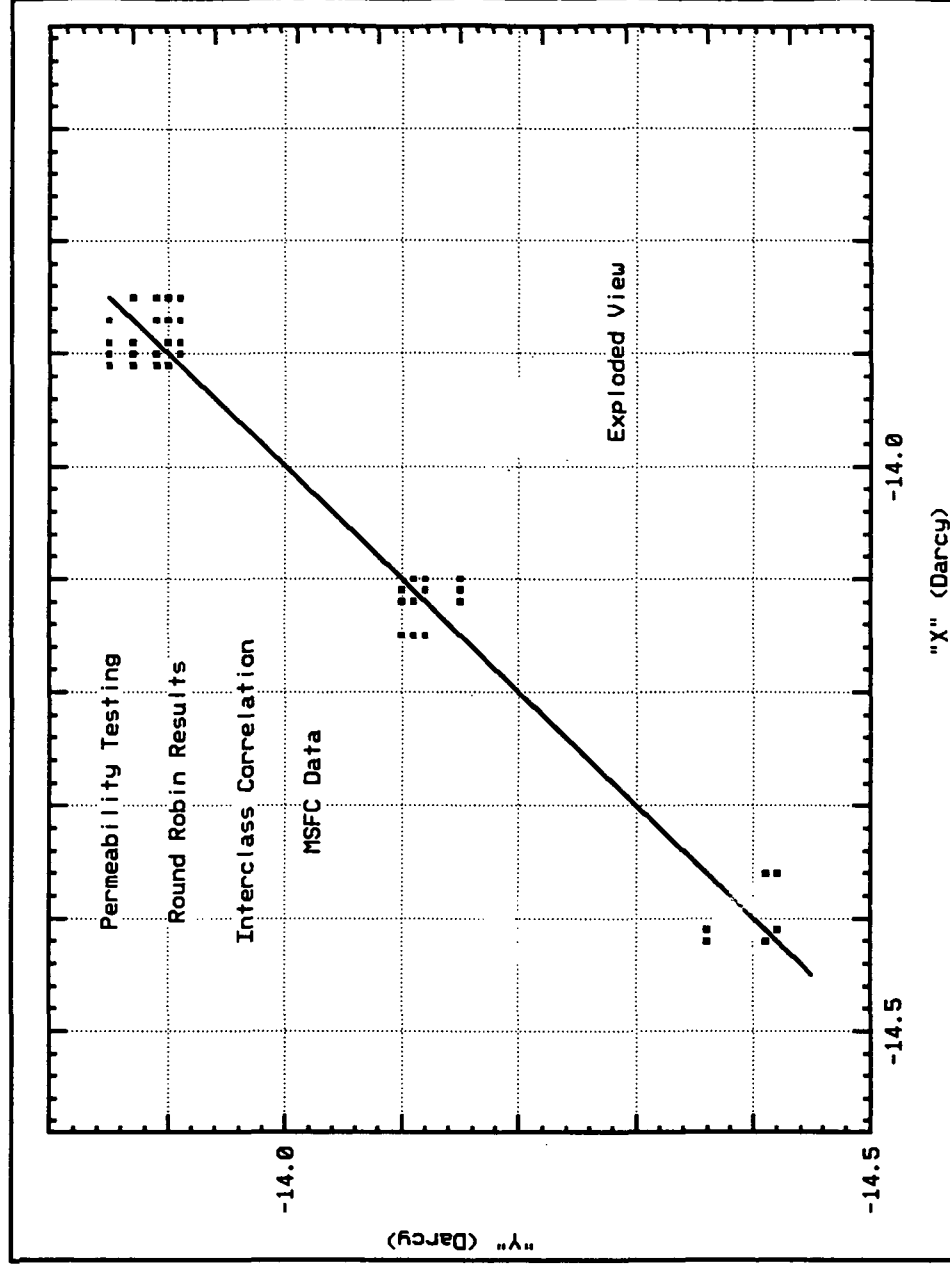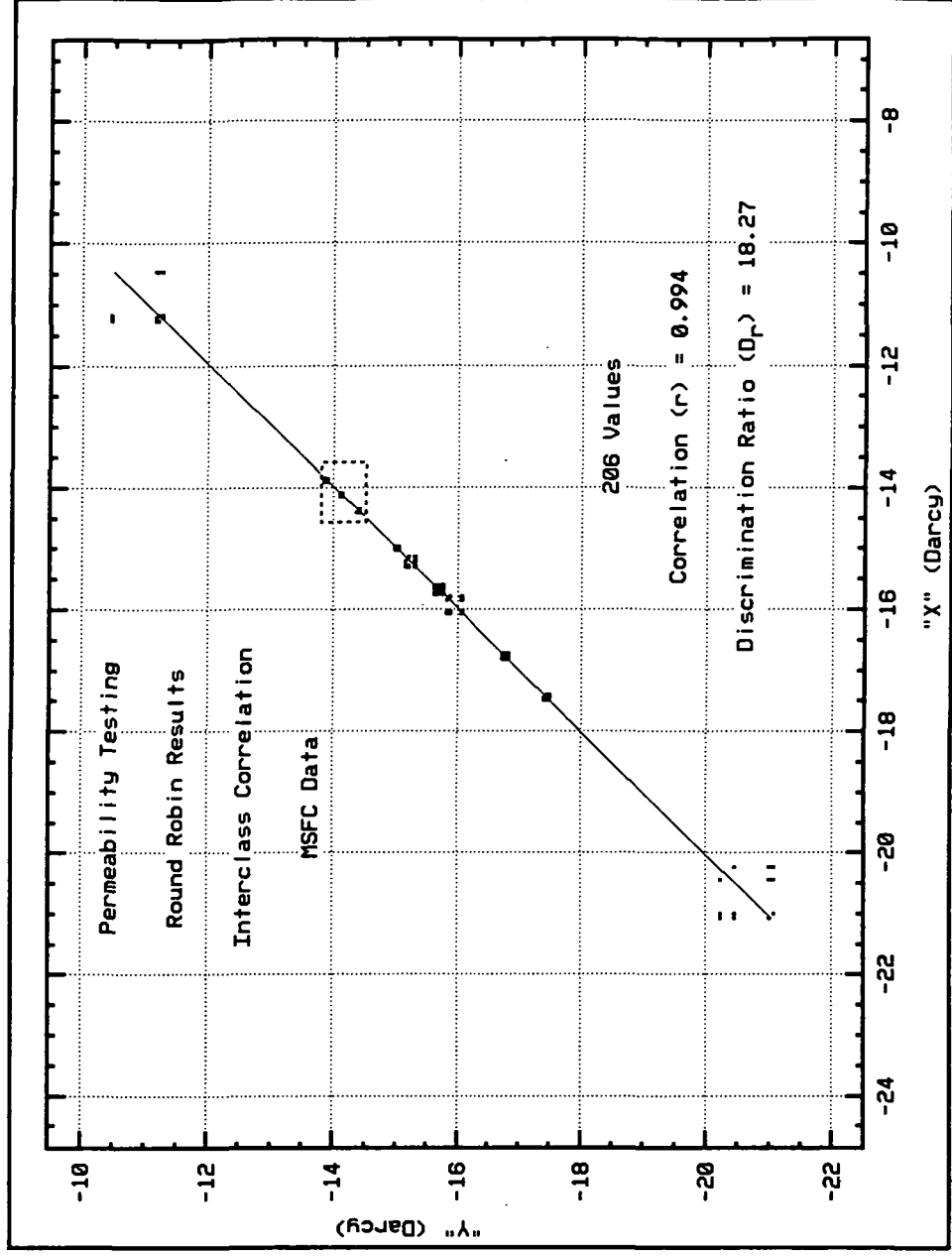
TOM FISHER

NMR Studies of Phenol-Formaldehyde Resins

and Related Compounds

Tom H. Fisher

Department of Chemistry

Mississippi State University

NMR OF PF RESINS

- Review of ^{13}C NMR Analysis of SC 1008 prepolymer Resin

- Extracted Prepreg Analysis

    — 5 Products of 4,4'-Dihydroxydiphenylmethane and Formaldehyde

    —11 Products of 2,4'-Dihydroxydiphenylmethane and Formaldehyde

    — Ring Types (A - G): Chemical Shift Ranges

    — Extraction Solvents

    — Analysis of MX 4926 and FM 5939

- Solids NMR

    — PF Resin

    — Composite
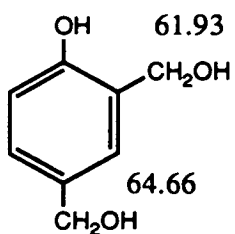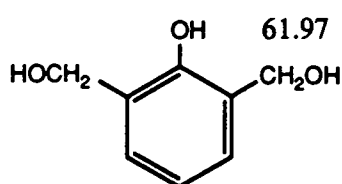
Assignments of Ipso and CH₂ carbons--PF resins

158.24

OH

1

157.28

OH

64.55
CH₂OH

2

156.15

OH   **61.86**
CH₂OH

3

155.18

OH   **61.93**
CH₂OH

64.66
CH₂OH

4

154.52

HOCH₂   OH   **61.97**
CH₂OH

5

153.65

HOCH₂   OH   **62.12**
CH₂OH

64.63
CH₂OH

6

OH   **156.36**

CH₂   **40.72**

OH

7

155.68
OH

CH₂   **35.39**

156.27
OH

8

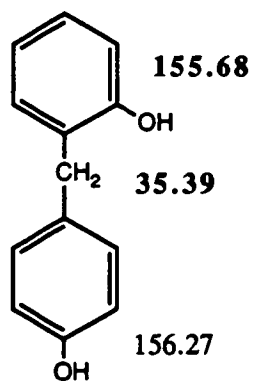Tom H. Fisher, MISSISSIPPI STATE UNIVERSITY

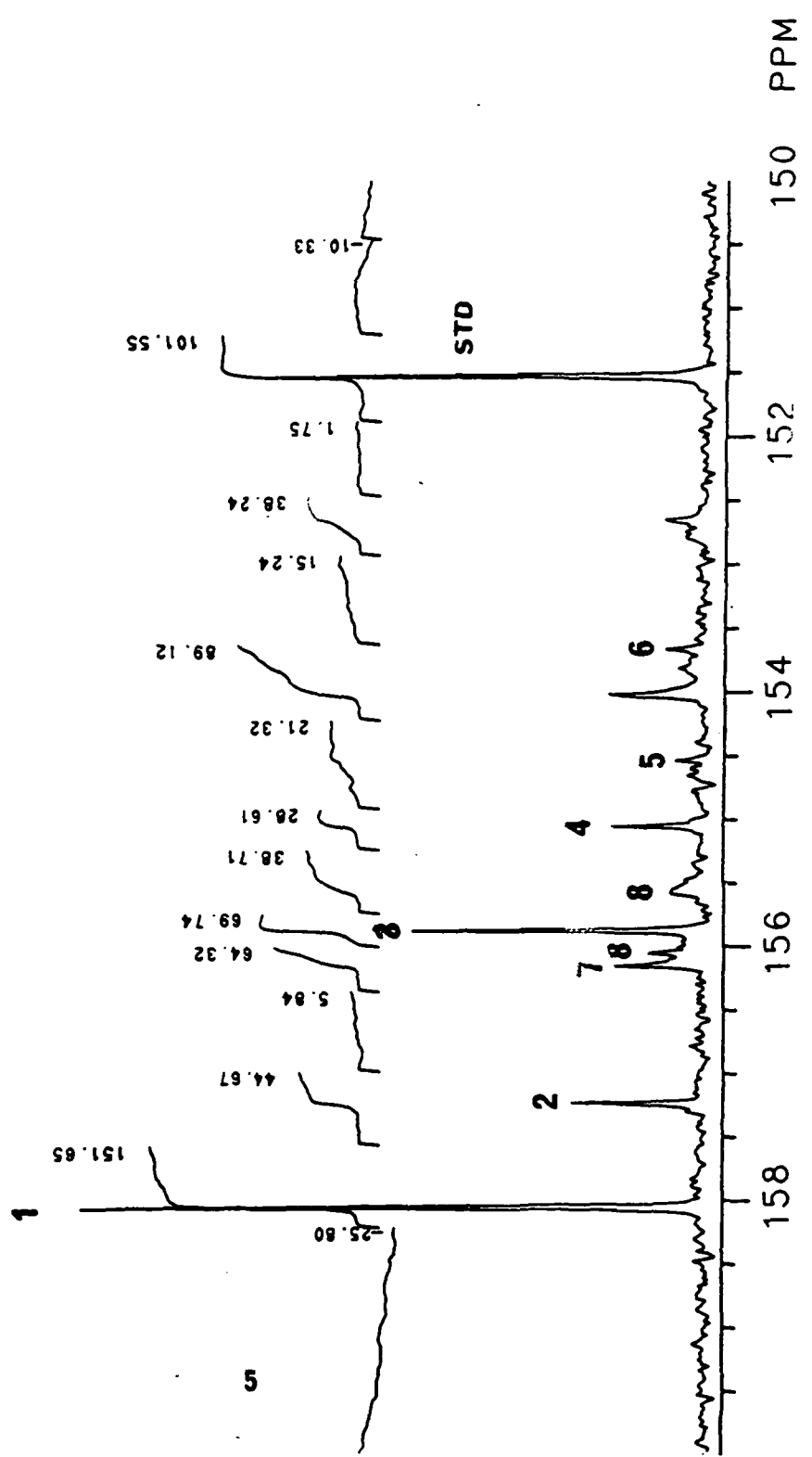# 13C CHEMICAL SHIFTS OF PF RESIN COMPONENTS

δ, ppm

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4

5.

SC 1008

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^{13}C NMR

151.65

1

44.67

5.84

64.32

69.14

38.71

28.61

21.32

89.12

15.24

38.24

1.75

101.55

STD

-10.33

-25.80

5

2

7

8

8

8

4

5

6

150 PPM

150

152

154

156

158
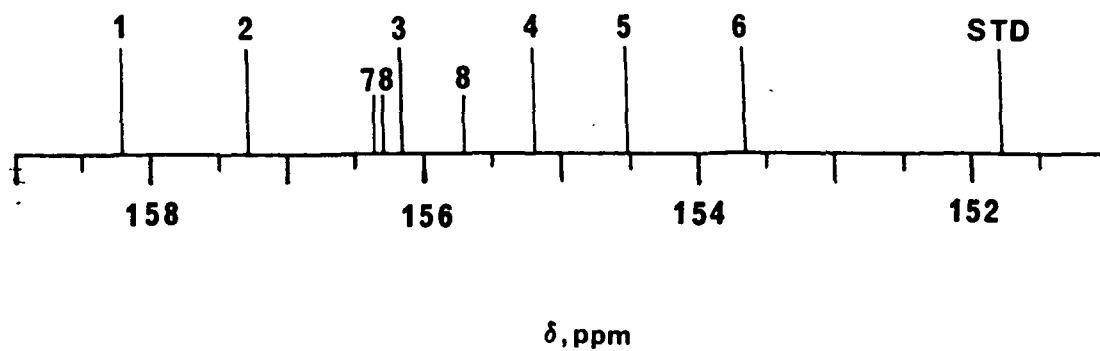
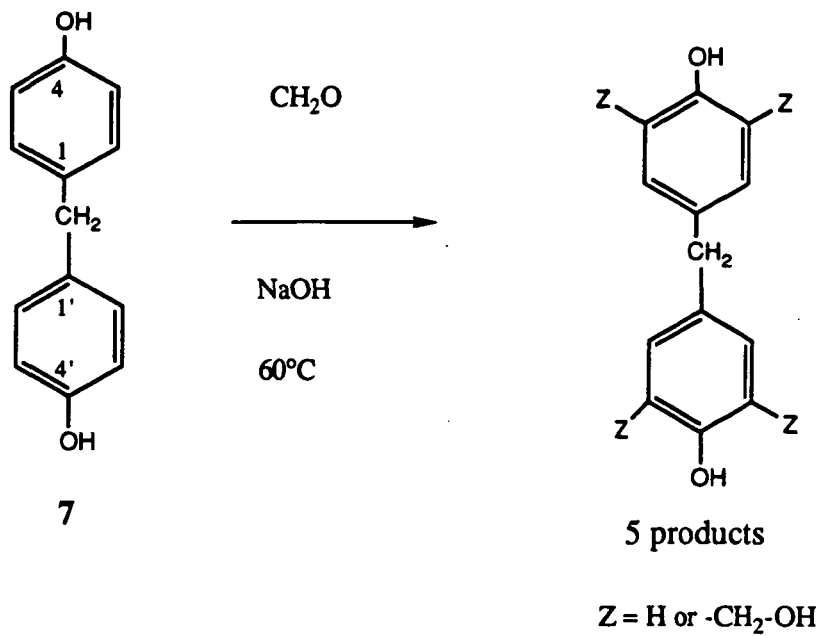# Reaction of 4,4'-(HOPh)$_2$CH$_2$ (7) and Formaldehyde

7

CH$_2$O

NaOH

60°C

5 products

Z = H or -CH$_2$-OH

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156.42

OH

CH₂

154.38   CH₂OH
OH

10

154.35

OH   CH₂OH

CH₂

154.35   CH₂OH
OH

11

152.82

HOCH₂   OH   CH₂OH

CH₂

156.42   OH

12

152.74

HOCH₂   OH   CH₂OH

CH₂

154.25   CH₂OH
OH

13

152.73

HOCH₂   OH   CH₂OH

CH₂

HOCH₂   CH₂OH
152.73   OH

14

156.36

OH

CH₂

OH   156.36

7

Reaction of 2,4'-(HOPh)$_2$CH$_2$ (8) and Formaldehyde

where:
Z = H or -CH$_2$-OH

11 products

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8   15   16   17

18   19   20   21*

22   23*   24*   25
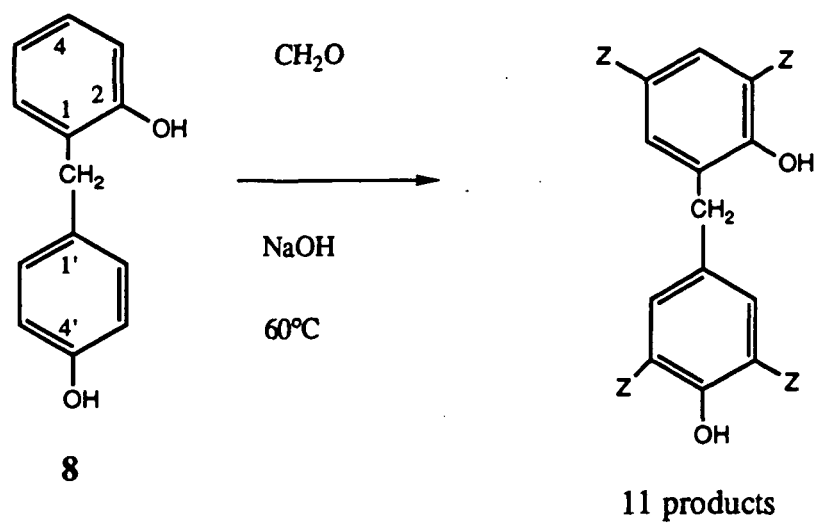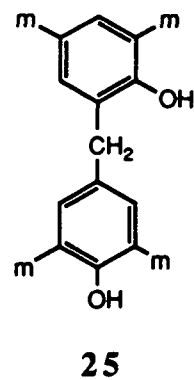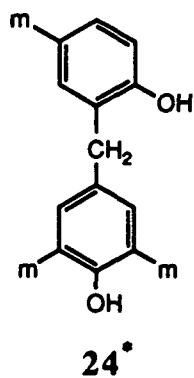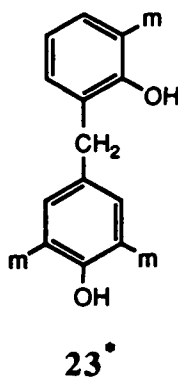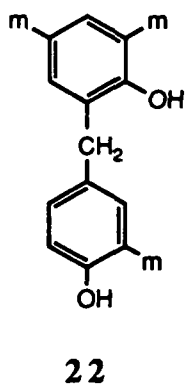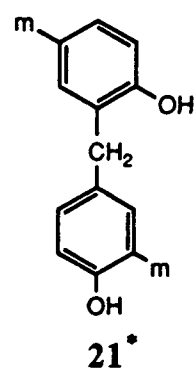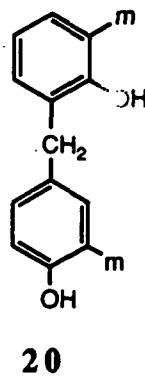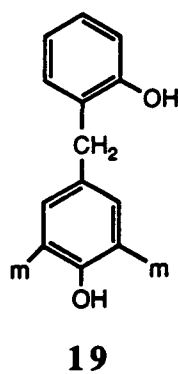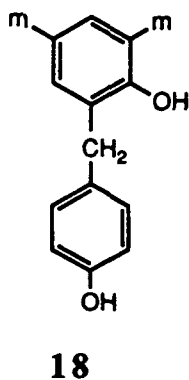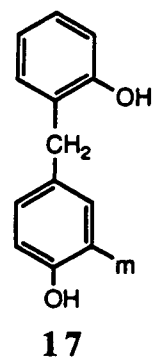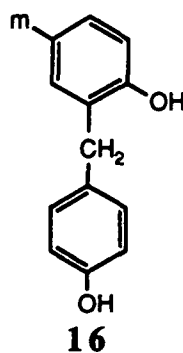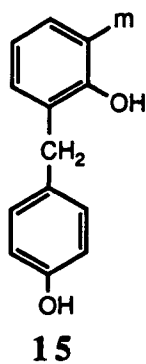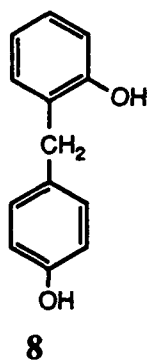
* Not isolated;   m = methylol

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9

Chemical Shifts (ppm) of Ipso Phenolic Carbons

155.58

155.02

154.79

156.27

8

156.39

15

156.26

16

153.95

153.87

154.35

22

152.74

25

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10
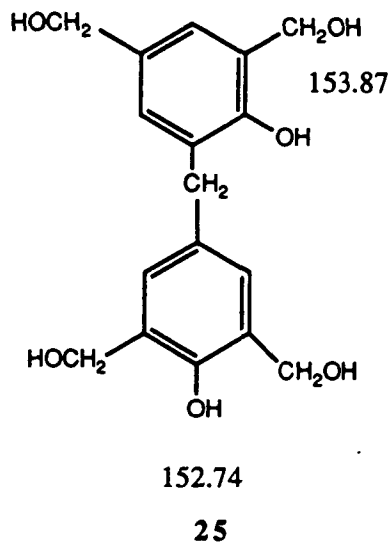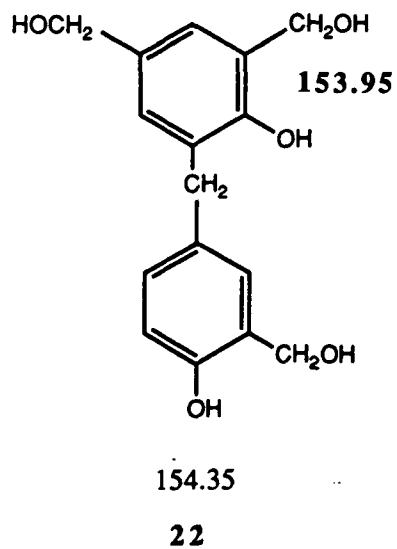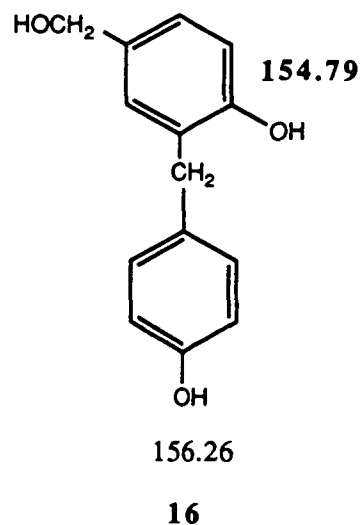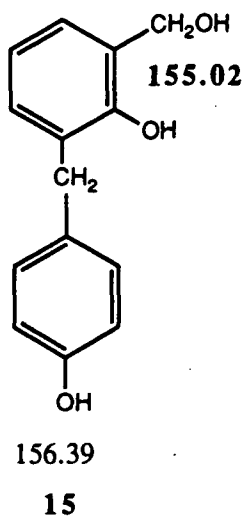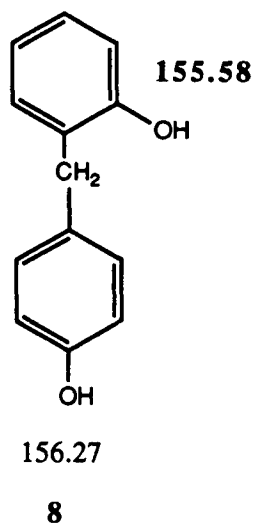
Substituted Ring Types Found in 4,4'- and 2,4'-Products

A
156.27 - 156.42
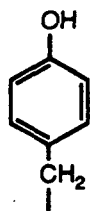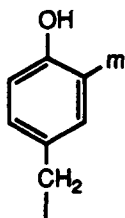
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25 - 154.37
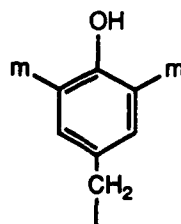
C
152.73 - 152.82
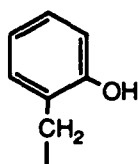
D
155.68 - 155.74
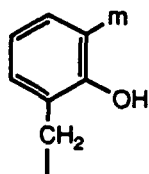
E
154.88 - 155.02
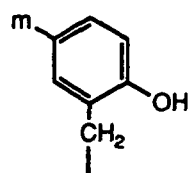
F
154.79
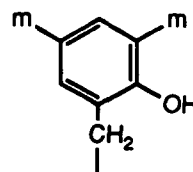
G
153.91 - 153.96

m = methylol = CH_2OH

Table 1. ^{13}C Chemical Shift Values (ppm) for the C-OH Phenolic Carbons in **10 - 25**.

Compd	4-Hydroxyphenyl Ring			2-Hydroxyphenyl Ring		
	Unsubst.	3-CH2OH	3,5-di-CH2OH	Unsubst.	3-CH2OH	3,5-di-CH2OH
4,4'- COMPOUNDS						
7	156.36					
10	156.42	154.38				
11		154.35				
12	156.42		152.82			
13		154.25	152.74			
14			152.73			
2,4'- COMPOUNDS						
8	156.27			155.68		
15	156.39				155.02	
17		154.32		155.74		
18	156.34					153.96
19			152.80	155.72		
20		154.21			154.88	
22		154.35				153.95
25			152.74			153.87
mean	156.37	154.31	152.77	155.71	154.95	153.93
±S.D.	0.06	0.07	0.04	0.03	0.10	0.05

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Table 2. ^{13}C Chemical Shift Values (ppm) for the Methylene and Methylol Carbons in 10 - 25.

Compd	ArCH2Ar	4-Hydroxyphenyl Ring		2-Hydroxyphenyl Ring		
		3-CH2OH	3,5-di-CH2OH	3-CH2OH	5-CH2OH[a]	3-CH2OH[a]
4,4'- COMPOUNDS						
7	40.72					
10	40.90	61.99				
11	41.07	61.95				
12	41.00		62.28			
13	41.05	61.73	62.18			
14	41.09		62.12			
	40.97±0.14					
2,4'- COMPOUNDS						
8	35.39					
15	35.12			64.22		
17	35.48	62.10				
18	35.20				64.61	64.33
19	35.53		62.36			
20	35.23	61.66		63.72		
22	35.28				64.61	64.30
25	35.32	___	62.26	___	64.56	64.11
mean±S.D.	35.32±0.14	61.89±0.18	62.24±0.09	63.97±0.35	64.59±0.03	64.25±0.12

[a]position in 3,5-dimethylol group

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Major Components of Prepreg PF Resin by NMR Analysis
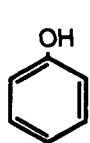
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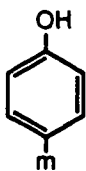
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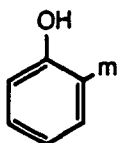
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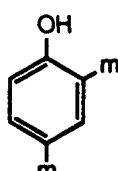
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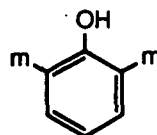
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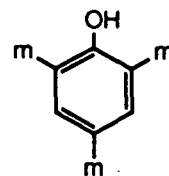
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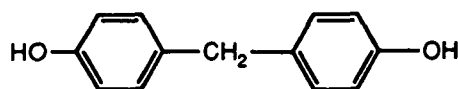
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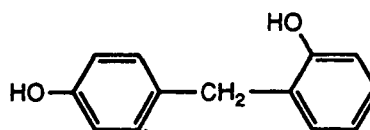
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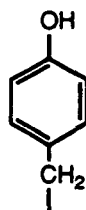
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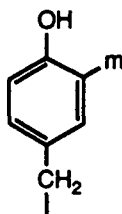
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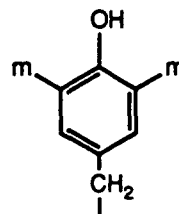
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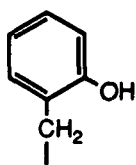
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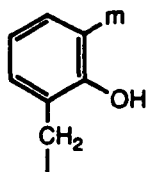
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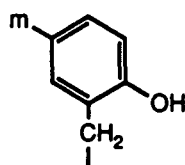
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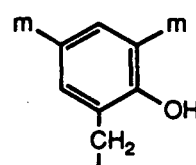
G

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14

¹³C CHEMICAL SHIFTS OF PF RESIN COMPONENTS

δ,ppm

15
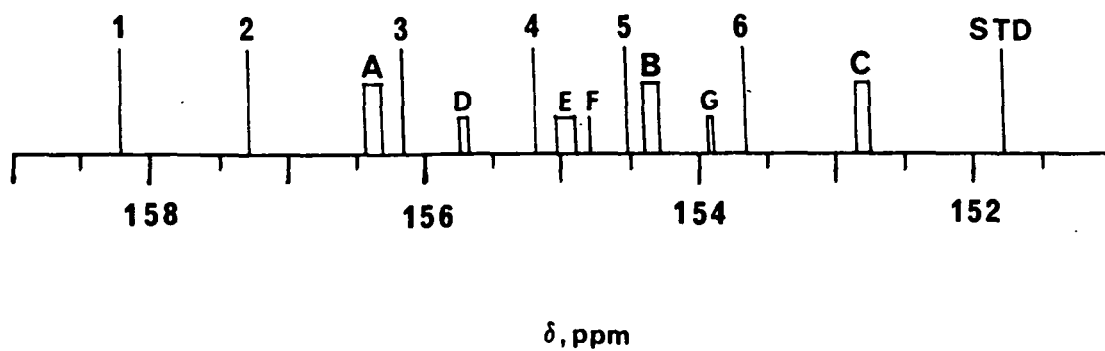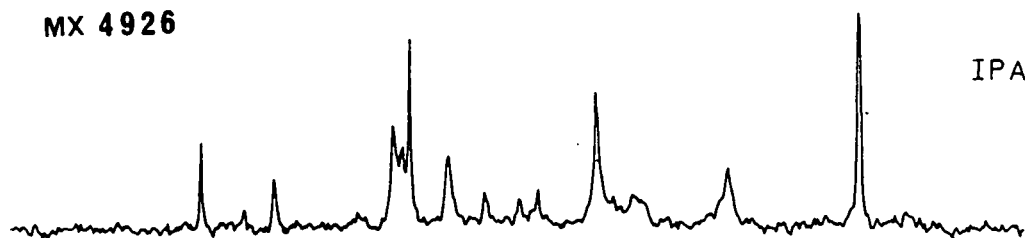
MX **4926**

IPA

METHANOL

ACETONE

160   158   156   154   152   150   PPM
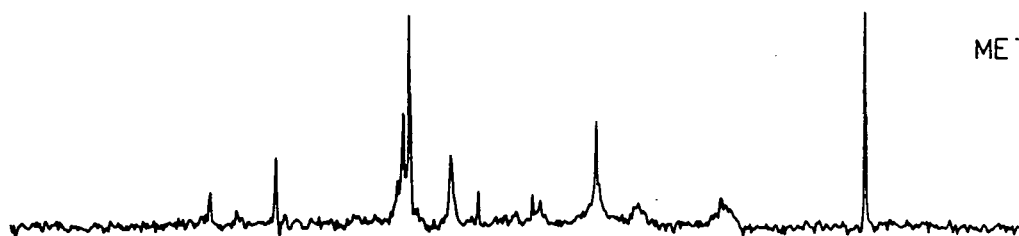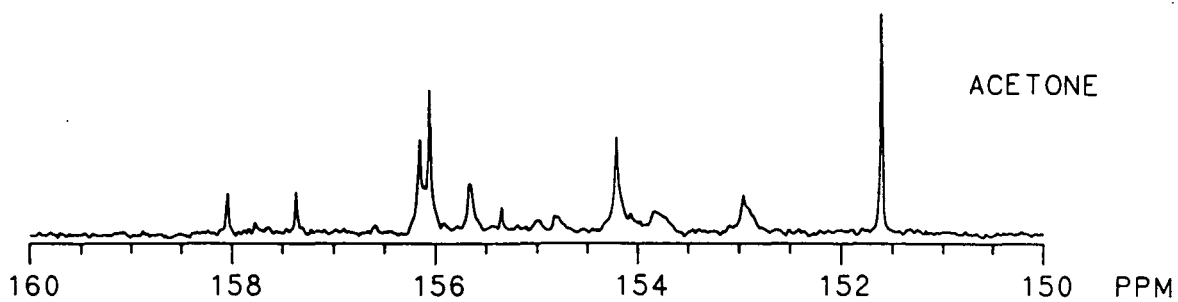
Table 3. NMR analyses of extracted Fiberite MX 4926 prepreg samples. See previous page for structures of compounds 1 - 8 and fragments A - G.

Found	EXTIP	EXTAC	M49A	EXTME	M49M	SC49GD	SPC3GD	Mean ± S. D.
1	3.5	3.5	4.6	4.4	4.8	4.0	5.0	4.3 ± 0.6
2	2.9	3.5	3.5	4.7	3.0	5.9	4.8	4.0 ± 1.1
3	12.9	10.4	12.1	15.3	11.4	11.1	11.5	12.1 ± 1.6
4	3.8	3.0	4.2	3.0	-	5.9	3.6	3.5 ± 1.9
6 & G	9.1	8.8	9.8	6.4	8.6	6.5	8.5	8.2 ± 1.3
7 & A	3.2	4.4	5.2	3.8	4.9	4.8	4.9	4.4 ± 0.7
8 & D	16.8	18.1	20.3	18.1	14.6	20.4	18.8	18.1 ± 2.0
B	18.0	18.0	18.5	17.5	16.9	18.4	15.7	17.6 ± 1.0
C	10.7	11.3	9.0	7.2	10.4	10.9	9.9	9.9 ± 1.4
E	2.6	3.0	2.8	2.4	4.3	2.7	2.4	2.9 ± 0.7
F	4.2	4.0	4.6	2.8	4.4	4.7	4.8	4.2 ± 0.7
Bn$_2$O	7.7	13.1	17.6	8.6	10.7	14.5	7.4	11.4 ± 3.8
-CH$_2$OH	45.3	40.0	37.4	41.6	40.0	54.6	54.4	44.8 ± 7.1
Amine	14.0	18.0	15.4	17.8	14.3	6.2	2.6	12.6 ± 5.9
ArCH$_2$Ar	33.0	29.0	29.7	32.1	35.1	24.7	35.6	31.3 ± 3.8
F / P	1.29	1.60	1.47	1.31	1.41	1.12	0.90	1.30 ± 0.2
% o-R	50.2	52.2	57.4	54.8	48.8	52.2	55.1	53.0 ± 3.0
% p-R	70.0	66.7	67.1	72.5	69.1	64.5	74.0	69.1 ± 3.3
solvent[a]	IPA	Acet	Acet	MeOH	MEOH	Acet	Acet	

[a]Extraction solvent. Acetone-d_6 was the NMR solvent used for all samples.

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Table 4. NMR analyses of extracted FM 5939 LDC prepreg samples. See earlier page for structures of compounds 1 - 8 and fragments A - G.

Found	PPREGD	PPG3B	91PPGD	Mean ± S. D.
1	6.8	5.9	6.1	6.3 ±0.5
2	12.3	9.9	11.9	11.4 ±1.3
3	10.3	10.9	9.6	10.3 ± 0.6
4	5.3	5.6	8.3	6.4 ± 1.6
6 & G	-	4.1	6.4	3.5 ± 3.2
7 & A	3.7	3.6	5.4	4.2 ± 1.0
8 & D	11.7	11.2	12.0	11.6 ± 0.4
B	6.3	10.0	10.5	8.9 ± 2.3
C	3.9	4.7	3.7	4.1 ± 0.5
Bn_2O	0.2	2.0	16.4	
$-CH_2OH$	27.8	39.4	36.0	34.4 ± 6.0
Amine	44.2	38.1	33.3	38.5 ± 5.5
$ArCH_2Ar$	29.3	20.7	13.9	21.3 ± 7.7
F / P	1.78	1.71	1.58	1.69 ± 0.1
% o-R`	53.9	52.2	49.6	51.9 ± 2.2
% p-R	61.6	59.1	56.0	58.9 ± 2.8
solvent[a]	Acet	Acet	Acet	

[a]Extraction solvent. Acetone-d_6 was the NMR solvent used for all samples.

Table 5. Comparison of NMR analyses of extracted Fiberite MX 4926 and extracted FM 5939 LDC prepreg samples.

	MX 4926		FM 5939 LCC	
I. AROMATICS				
1	4.3 mole %		6.3 mole %	
2	4.0		11.4	
3	12.1		10.3	
4	3.5	(cum. 23.9%)	6.4	(cum. 34.4%)
6 & G	8.2		3.5	
7 & A	4.4		4.2	
8 & D	18.1		11.6	
B	17.6		8.9	
C	9.9		4.1	
E	2.9		-	
F	4.2	(cum. 65.3%) (cum.total 89.2%)	- (cum. 32.3%)	(cum. total 66.7%)
II. METHYLENES				
Bn2O	11.4		6.2	
-CH2OH	44.8		34.4	
Amine	12.6		38.5	* major difference
ArCH2Ar	31.3		21.3	
III. OTHER				
F / P	1.3		1.7	
% o-R	53		52	
% p-R	69		59	

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PF resin from Tony Day
10 kHz MAS

Tom H. Fisher, MISSISSIPPI STATE UNIVERSITY

m-CH
o-,p-CR
OH

o-,p-CH

ArCH₂Ar

ArCH₂OH

OH
C

ppm 150 125 100 75 50 25

20
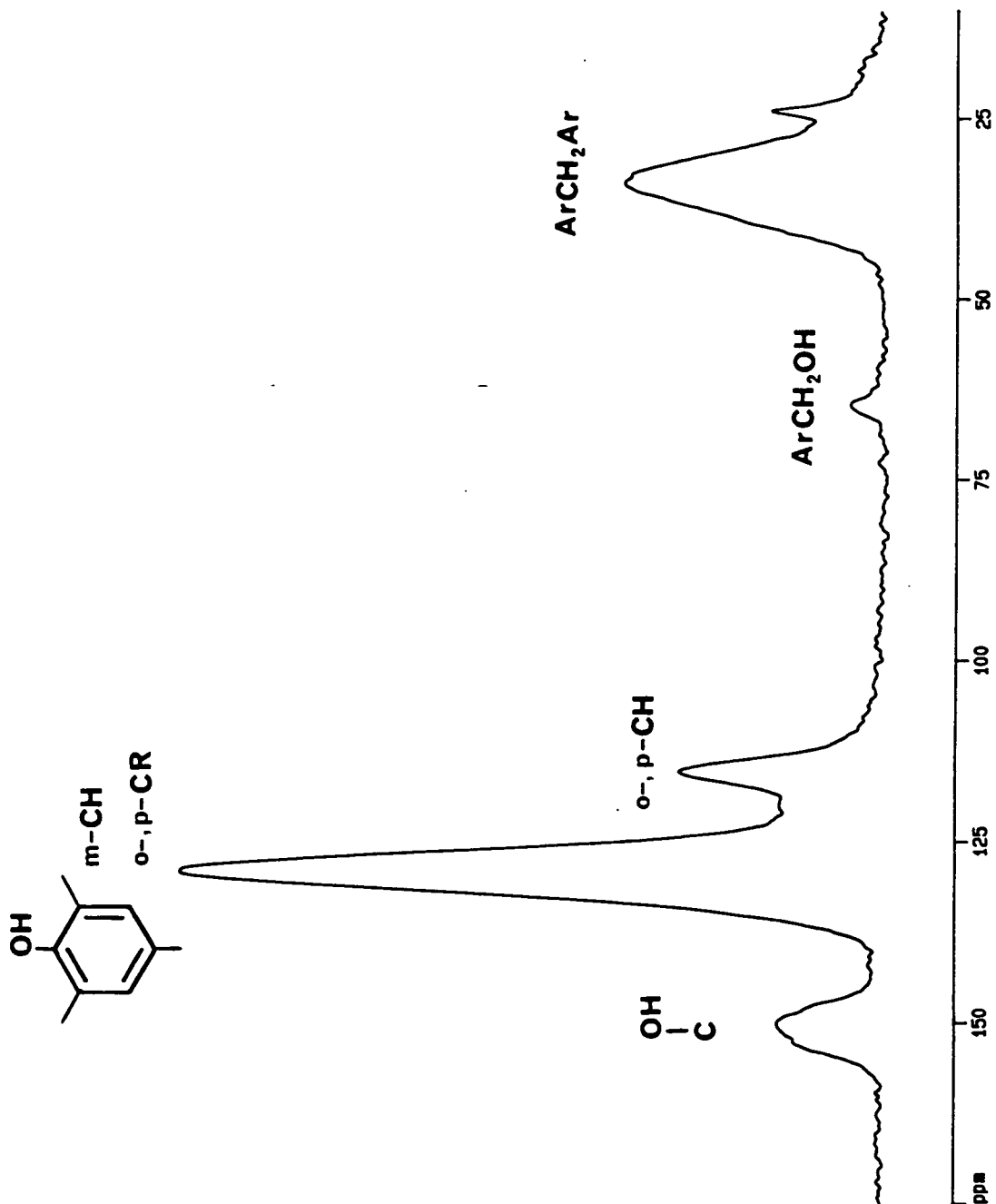
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12 kHz MAS; ns = 6000

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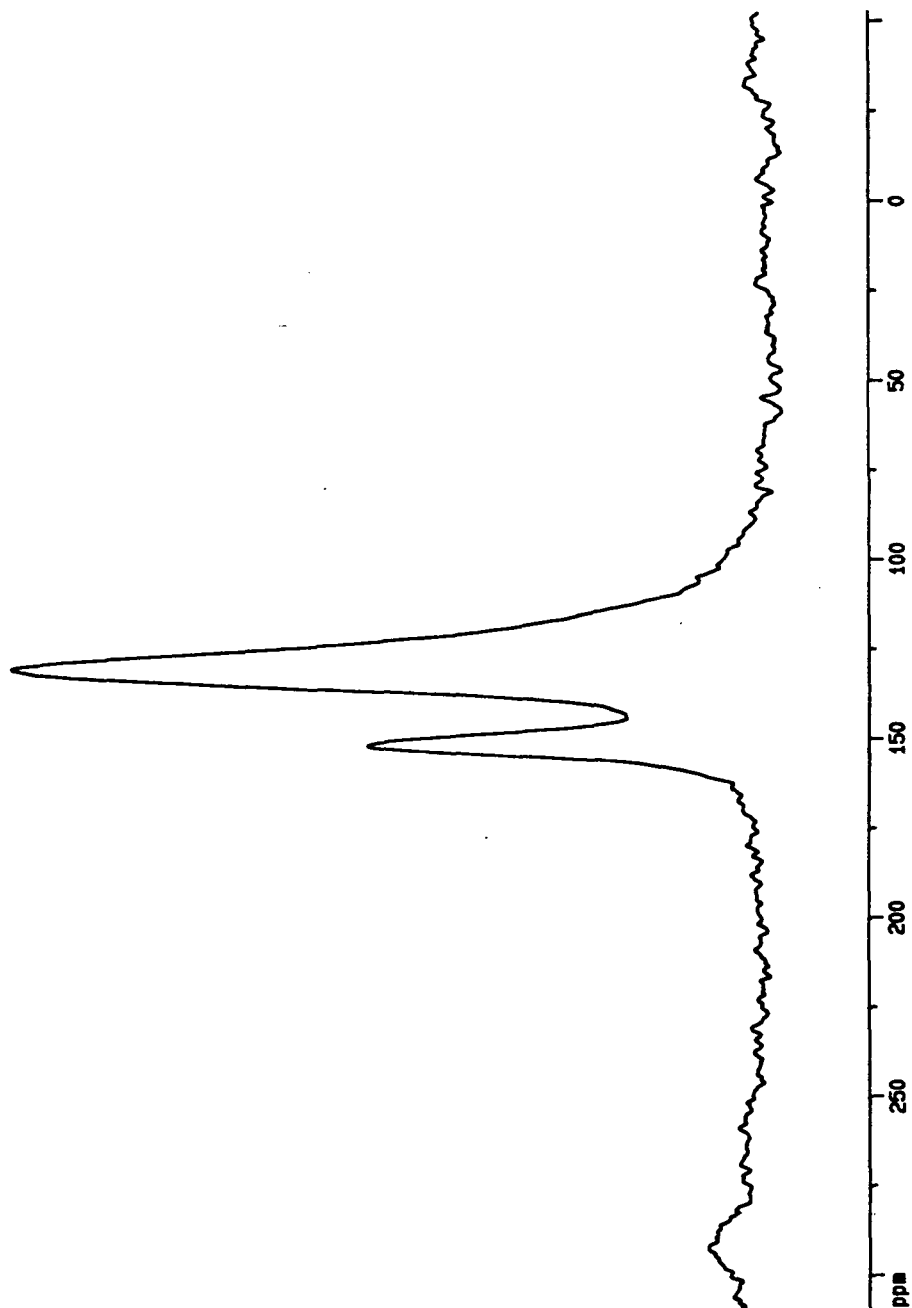
ACKNOWLEDGMENTS

Ping Chao

NASA - Huntsville

Hercules Aerospace

State of Mississippi: QE-300 NMR Spectrometer

R&DD

Lockheed

LDC

CONSTITUENT TESTING HIGHLIGHTS

Presented to the
12th Biannual IAC Meeting
Mississippi State University
Starkville, Mississippi
May 19, 1994

D. Beckley, BP/Chemicals
P. Pinoli, Lockheed R&DD
R. Shaver, Carbospheres

LDC
CONSTITUENT TESTING HIGHLIGHTS ☆Lockheed

OBJECTIVE

● **Conduct comprehensive testing of constituent materials employed on Phase 1 of the NASA funded "FM-5939 LDC Optimization Program."**

● **Compare Carbospheres Type "A" vs. Type "T" carbon balloon properties.**

Type "A" The entire DoD program data base on LDC prepreg is based on this product.

Type "T" High purity version of Type "A" purchased for the ASRM program (5,000 #)

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CONCLUSIONS

Carbon Fabric

- Rayon based CCA8+ fiber properties were consistent with the data base at LPARL and BP Chemicals. Analyses performed were:

    - SEM Surface Condition

    - XPS surface Analysis

    - Surface Area

    - Air Oxidation Sensitivity

    - Moisture Adsorption

CONCLUSIONS

Carbon Filler

● Shawinigan carbon black properties were consistent with conventional carbon black properties. Analyses perfo... were:

- SEM Particle Appearance

- XPS Surface Analysis

- Surface Area

- Air Oxidation Sensitivity

- Moisture Adsorption

- Apparent Density

- Apparent Stiffness

CARBON BALLOONS FOR
LOW DENSITY CARBON PHENOLIC

APPROACH

- Type "A" vs. Type "T"

    - Compare acceptance data

    - Conduct non-routine analysis

- Characterize "active state" of carbon for reference

- Assess adequacy of acceptance tests and methodology

CARBON BALLOONS FOR
LOW DENSITY CARBON PHENOLIC
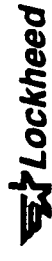
Specification Requirements

Physical Property	Type "A"	Type "T"
Bulk Density, g/cm^3	<0.23	<0.23
Sieve Analysis	98% thru 50 mesh 25% max thru 325 mesh	98% thru 50 mesh 25% max thru 325 mesh
Volatiles, w% (2 hours @ 100°C)	2% max	2% max
Ash Content, w%	4% max	1% max
Moisture Adsorption, w% (24% ambient temperature, 100% RH)	-	Report only
Floater/Sinkers	-	Report % Sinkers

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CARBON BALLOONS FOR
LOW DENSITY CARBON PHENOLIC

Type "A" vs Type "T" Statistical Analysis

	Ash Content, %		Volatiles, %		Tapped Bulk Density, g/cc		Methanol Sinkers, %		% through 325 mesh		% through 50 mesh	
	avg	median	avg	median	avg	median	avg	median	avg	median	avg	median
Type T	0.65	0.65	0.32	0.22	0.186	0.186	29.2	28.8	22.1	22.3	99.7	99.8
Type A	2.07	2.04	0.48	0.38	0.184	0.184	26.9	27.7	21.6	22.1	99.6	99.7

Sample Size   102 Lots of Type T (5,000 lbs)

557 Lots of Type A (27,850 lbs), except Sinkers on 348 of the 557 Lots

Reference - Carbospheres, Inc.

ASH CONTENT

Total Production Distribution for Type "A" and Type "T"

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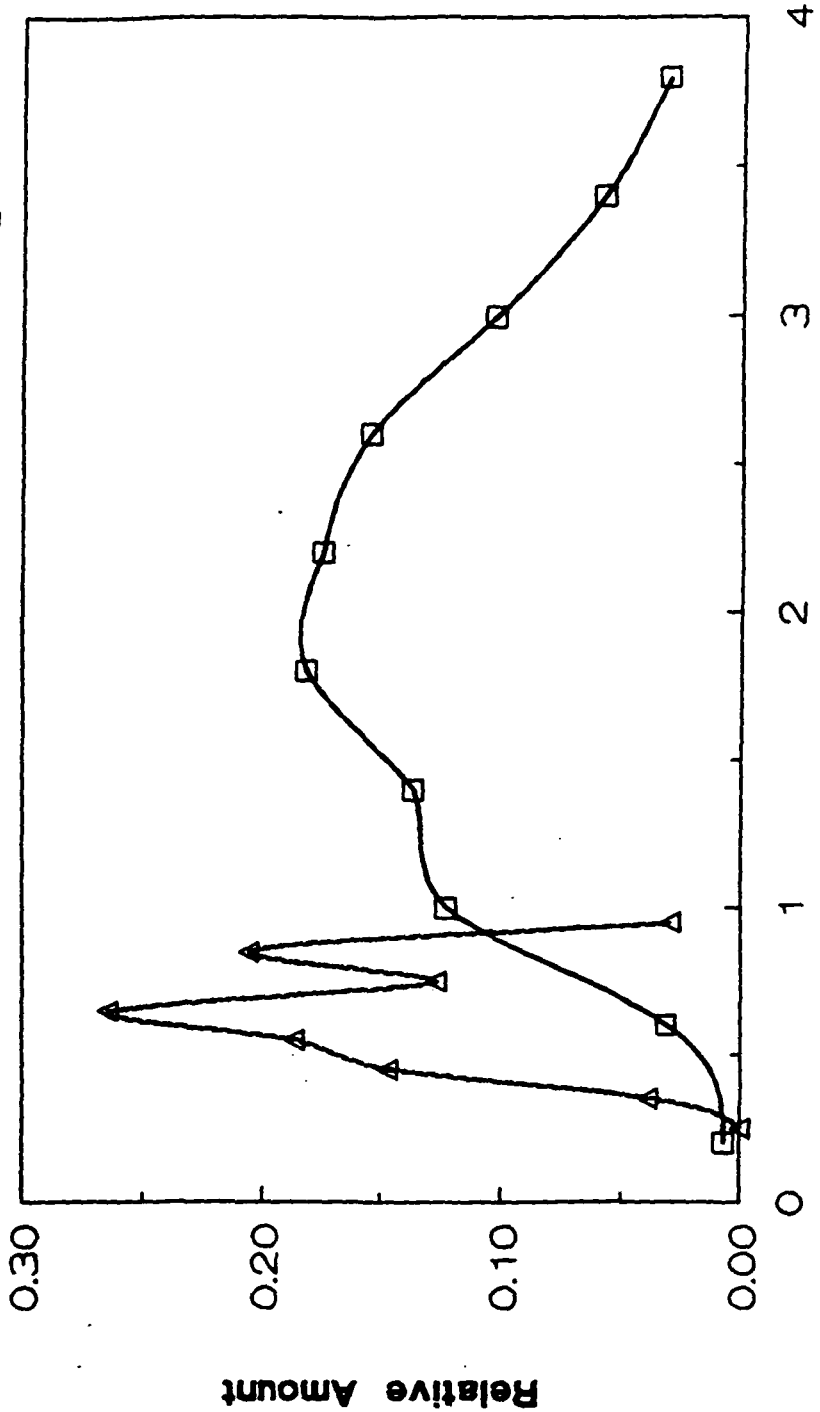
**CARBON BALLOONS FOR
LOW DENSITY CARBON PHENOLIC**

MOISTURE ADSORPTION

Total Production of Type "T" and 10 Lots of Type "A"

□ Type A   + Type T

Percent Moisture Pickup

Relative Amount
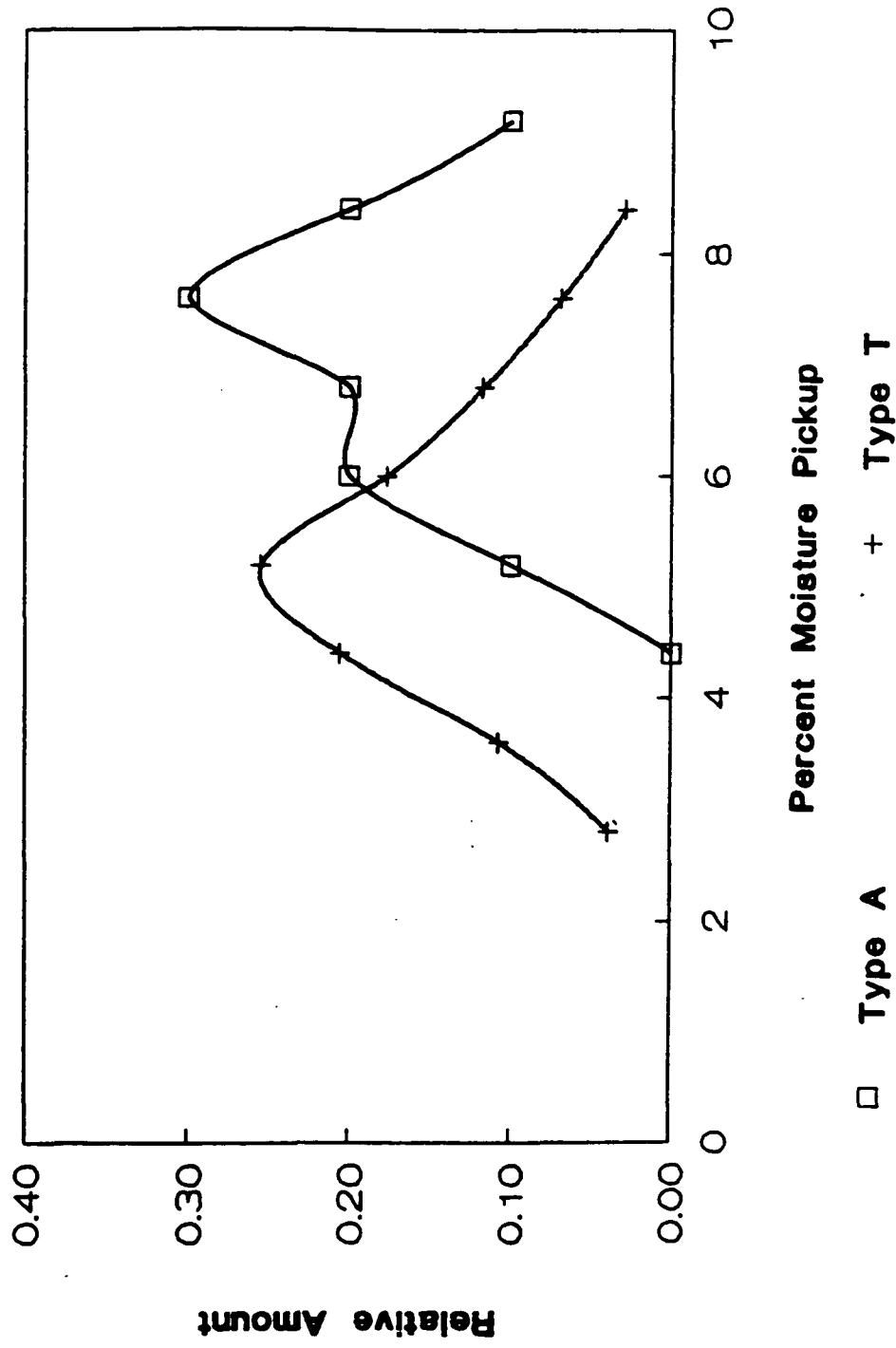
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CARBON BALLOONS FOR
LOW DENSITY CARBON PHENOLIC

SPIP Activity
Relationship of Ash to Na Level
in Carbon Fabric and Microballoons

LEGEND
□ microballoons
O carbon fabric

Na, ppm

Ash, w%
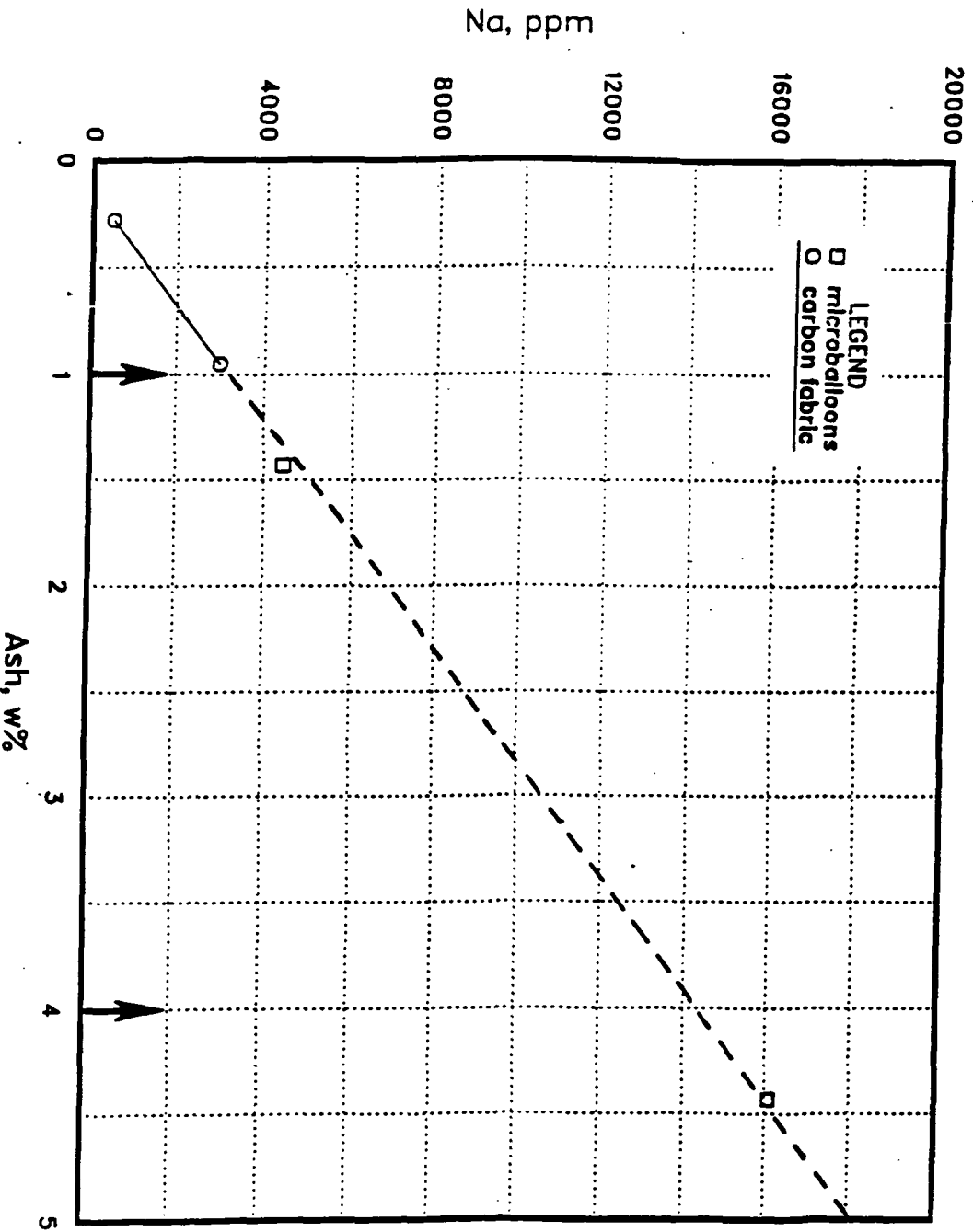
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LOW DENSITY CARBON PHENOLIC

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Arrhenius Plots for Air Oxidation Mass Loss
LDC Constituent Testing

k (10^{-5} g/g-sec) vs **Temperature °C**

LEGEND

□ = Type "A" Lot LWA 181-11
o = Type "A" Lot LWA 182-06
Δ = Type "T" Lot LWT 190-03
+ = Type "T" Lot LWT 190-04
x = CCA8 + Roll 4263-2A
◇ = Carbon Black Filler (RN 46222)
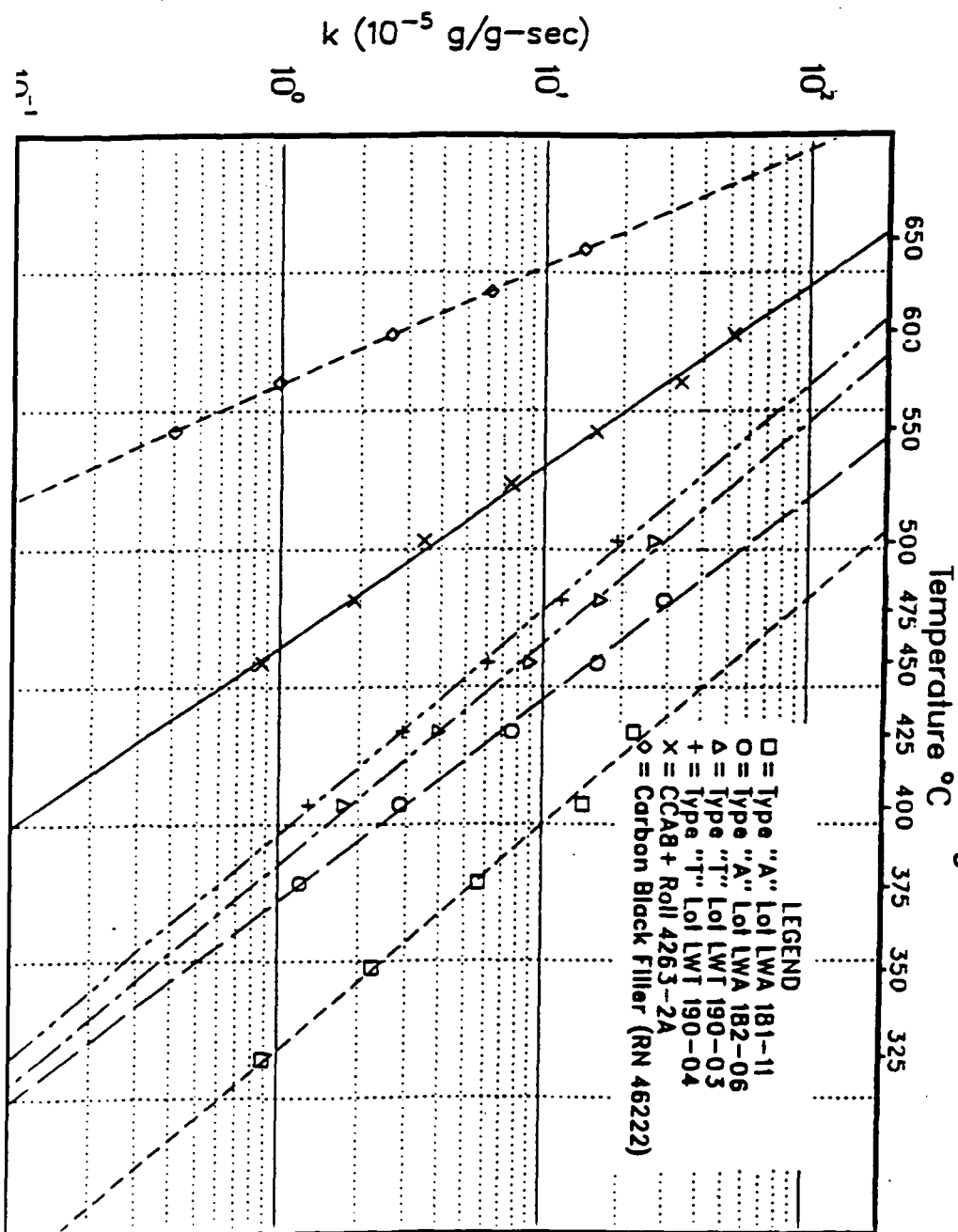
CARBON BALLOONS FOR
LOW DENSITY CARBON PHENOLIC

Surface Area of Type "A" and Type 'T'

Carbon Balloon	Surface Area, m²/g			
	N$_2$ Adsorbate		CO$_2$ Adsorbate	
	A/R	Ground	A/R	Ground
Type "A"				
LWA 182-02	35.7	38.0	46.1	30.6
BP/Chemicals	45.0	25.6	52.3	42.9
(ASRM Task 3 Lot 1 Bottom)				
Type 'T'				
LWT 190-02	35.6		64.8	71.6
LWT 190-03	25.5	35.9	70.8	
LWT 190-04	27.4	34.9	96.4	120.3
LWT 190-04 rerun			92.6	
LWT 190-05	41.4		209	
Reference Carbon				
Conventional PAN	1	-	1	-
Based Fiber (T-300, AS-4)				
Low Fired Rayon 59-72	-	-	500-1,186	-
Based Fiber (CCA3, CSA)				

CARBON BALLOONS FOR
LOW DENSITY CARBON PHENOLIC

XPS Elemental Analysis of Type 'T' Carbon Balloons

Element	Carbospheres LWT 190-03 atom %	Carbospheres LWT 190-04 atom %
C	93.8	94.4
O	4.7	4.2
Na	1.3	1.2
Si	0.1	0.1
S	0.04	0.02
Cl	0.03	0.03

Reference BP/Chemicals

CARBON BALLOONS FOR
LOW DENSITY CARBON PHENOLIC

Auger Elemental Analysis of Type "T" Carbon Balloons

	Carbospheres LWT 190-03		Carbospheres LWT 190-04		
	Area 1	Area 2	Area 1	Area 2	Area 3
	No Flakes	Flakes	Interior	Flakes	No Flakes
Composition (at%)					
C	96.44	44.26	95.53	87.58	94.63
O	1.33	22.49	1.62	3.68	2.05
Na	1.38	31.02	2.32	6.56	2.59
S	0.85	2.23	0.53	2.18	0.74

Reference - BP/Chemicals

Ash/Na Levels in Study Carbon

Pathfinder Lots	Ash, w%	Re-Run	Na, ppm (est)	Re-run
A/R				
LWT 190-03	0.64		1800	
LWT 190-04	0.59		1600	
A/R Acid Washed				
LWT 190-03	0.18	0.08	200	<100
LWT 190-04	0.47	0.18	1200	200
Ground & Purified @ Carbospheres				
LWT 190-03	0.54		1400	
LWT 190-04	0.42		980	
Ground/Purified & Acid Washed				
LWT 190-03	0.30		520	
LWT 190-04	0.11		<100	
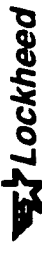
CARBON BALLOONS FOR
LOW DENSITY CARBON PHENOLIC

Type "A" % Sinkers and Organic Liquids Properties

Organic Liquid	Dipole Moment x 10^{18} esu	Viscosity cp	Surface Tension dynes/cm	v % Carbon Sinkers
% Sinkers Range				
1 Very Low				
Carbon Tetrachloride	0	1.04	27.0	0.7
Methylene Chloride	1.54	0.45	26.5	2.6
2 Low				
Benzene	0	0.71	28.9	5.2
Hexane	0	0.41	18.4	6.6
3 Intermediate				
Isopropanol	1.60	2.86	21.7	20.6
Methanol	1.70	0.62	22.6	22.2
Acetone	2.89	0.34	23.7	23.6
4 High				
Ethyl Ether	1.15	0.25	17.0	45.7

Reference - Carbospheres, Inc.

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CARBON BALLOONS FOR
LOW DENSITY CARBON PHENOLIC

Type "A" % Sinkers and Organic Liquid Density

% Sinker Range		Organic Liquid	Liquid Density, g/cc	v % Carbon Sinkers
1	Very Low	Carbon Tetrachloride	1.60	0.7
		Methylene Chloride	1.34	2.6
2	Low	Benzene	0.88	5.2
		Hexane	0.66	6.6
3	Intermediate	Isopropanol	0.79	20.6
		Methanol	0.80	22.2
		Acetone	0.79	23.6
4	High	Ethyl Ether	0.71	45.7

CONCLUSIONS

Carbon Balloons

- Acceptance specification data on Type "A" vs. Type "T" indicate
  - Bulk density values are comparable
  - Sieve analysis values are comparable
  - Volatile content values are comparable
  - Ash content of "T" is much lower than "A" (lot averages 0.65 vs. 2.07 w%)
  - Moisture adsorption of Type "T" is significantly lower than "A".
  - Lot distribution of percent sinkers data is narrower for Type "T". Both "A" and "T" reflect Gaussian lot data distribution.

- Non-routine testing of Type "A" vs. Type "T" indicate
  - Long term moisture adsorption pickup for Type "T" is lower than Type "A"
  - Measured CO_2 surface areas of Type "T" product were higher than Type "A". This difference however may not be significant if more lots of Type "A" are tested.
  - Measured N_2 surface areas for Type "A" and Type "T" are comparable
  - Air oxidation sensitivity data indicates the mass loss rate of Type "A" product is much higher than Type "T".
  - The SEM surface characteristics of Type "A" and Type "T" are comparable.

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CONCLUSIONS

Carbon Balloons (continued)

● Surface and fundamental analysis

  ▪ SEM/EDAX elemental analysis indicated no relationship of residual Na to surface flake condition.

  ▪ XPS and Auger elemental analysis indicate in most spot regions studied, higher levels of Na are present in flake regions as opposed to clean/smooth carbon balloon surfaces.

  ▪ EDAX vs. XPS/Auger analysis indicates Na levels vary significantly from a few atoms on the surface (XPS/Auger) to more in depth (EDAX) assessment of Na levels.

  ▪ The Auger analysis confirms relatively high levels of surface oxygen (4-5 atomic %). Chemisorbed oxygen confirms the "activated" state of all carbon balloons studied and the measured moisture adsorption pickup values.

● The residual Na is not located inside of carbon balloons.

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Formulation Criteria for Phase I Prepregs

Expt'l Run Number	Elastomer %	Micro-Balloons %	Carbon-Black %	Resin %	Fabric %	Fabric H.T. F	Resin Advance
10–1	4.0	12.0	0.3	33.7	50.0	2450	Normal
10–2	4.0	12.0	0.3	33.7	50.0	2450	Normal
15–1	2.7	7.0	0.3	35.0	55.0	2450	Normal
15–2	2.7	7.0	0.3	35.0	55.0	2450	Normal
16–1	4.7	5.0	0.3	30.0	60.0	2450	Normal

Phase I BP Chemical Panel Data

Run Number	Prepreg Lot Number	Residual Volatiles %	Tensile Strength Fill,RT, psi	Tensile Elongation Fill,RT, %	Interlam 2xNotch Shear psi
10–1	RT01707	3.06	7243	1.2	1919
10–2	RT01708	2.63	6823	1.3	2003
15–1	RT01709	2.98	8905	1.4	2501
15–2	RT01710	2.67	8221	1.2	2441
16–1	RT01711	3.58	11910	1.3	2017

Karl Fischer Analysis of Residual Volatile Level in 91LD Resin and Premix Formulation 15

Identification	Temperature °F	w% loss	w% H_2O	water ratio
Resin	500	34.4	12.7	0.37
91LD	500	33.2	12.9	0.39
Rec No 46222	500	34.4	13.0	0.38
P/N 109152	500	34.0	12.9	0.38
x	500	0.7	0.2	0.01
•				
	325	27.7	12.9	0.47
	325	29.1	13.2	0.45
	325	28.9	13.2	0.46
	325	28.6	13.1	0.46
x	325	0.8	0.2	.01
•				
Resin Premix	500	34.0	9.3	0.27
DR 06557 (15-1)	500	35.1	9.9	0.28
F5081T Mod.	500	34.2	8.8	0.28
	500	34.3	9.3	0.27
x	500	0.5	0.6	0.01
•				
	325	34.5	9.8	0.28
	325	29.2	10.2	0.35
	325	31.0	8.7	0.28
	325	31.6	9.6	0.30
x	325	2.7	0.8	0.04
•				

2 hours at temperature

Karl Fischer Analysis of Residual Volatile Level in Prepreg Lots 10-1, 15-1 and 16-1

prepreg	Temperature °F	w% loss	w% H_2O	water ratio
RTO 1707-1 Run 10-1	500	6.86	3.06	0.45
	500	7.70	4.21	0.55
	500	7.28	3.64	0.50
	500	0.59	0.01	0.07
	325	5.82	2.32	0.40
	325	5.81	4.17	0.72
	325	5.72	4.50	0.79
	325	5.78	3.64	0.64
		.06	1.18	0.20
RTO 1709-2 Run 15-1	500	6.83	3.46	0.51
	500	7.19	3.66	0.51
	500	7.01	3.56	0.51
		0.25	0.14	0.00
	325	5.00	2.16	0.44
	325	5.44	2.86	0.53
	325	5.22	2.51	0.49
		0.31	0.50	0.06
RTO 1711-1 Run 16-1	500	6.93	3.09	0.45
	500	7.10	4.29	0.60
	500	6.65	4.16	0.63
	500	6.89	3.65	0.58
		0.23	0.66	0.10
	325	5.26	1.90	0.36
	325	5.82	2.54	0.44
	325	5.54	2.22	0.40
		0.40	0.45	0.06

2 hours at temperature

Karl Fischer Analysis of Residual Volatile Level in Cured Panels

panel	Temperature °F	w% loss	w% H_2O	water ratio
10-1	500	4.29	1.50	0.35
	500	2.95	1.44	0.49
	500	2.81	1.53	0.54
	500	3.35	1.49	0.48
•		0.82	0.05	0.10
	325	1.53	1.20	0.79
	325	1.53	1.26	0.83
	325	1.63	1.27	0.78
✶	325	1.56	1.24	0.80
•		0.06	0.04	0.03
15-1	500	2.97	1.87	0.63
	500	3.44	2.18	0.63
	500	3.38	2.11	0.62
✶	500	3.26	2.05	0.63
•		0.26	0.16	0.05
	325	1.71	1.66	0.97
	325	2.11	2.13	1.01
	325	1.95	1.80	0.92
✶	325	1.92	1.86	0.97
•		0.20	0.24	0.04
16-1	500	3.33	1.93	0.58
	500	2.96	1.73	0.58
	500	3.71	2.40	0.65
✶	500	3.33	2.02	0.60
•		0.38	0.34	0.04
	325	1.97	1.92	0.97
	325	2.33	1.93	0.83
	325	3.09	2.60	0.84
✶	325	2.46	2.15	0.88
•		0.57	0.39	0.08

2 hour

CONCLUSIONS

Karl Fischer Analysis

• Residual volatiles analysis of neat resin (60% resin solids 91LD) and the premix indicate higher moisture evolution at 500 °F vs. 325 °F is due to the inability of moisture to diffuse out of the resin as opposed to additional condensation reaction.

• At least 5 samples must be run on prepreg to obtain representative residual volatile values; due to the inherent Karl Fischer analysis specimen size limitation (0.6 in^2).

• Variability of measured residual volatiles in panels was extremely high and attributed to non-uniformity of porosity distribution present in each panel. Panel porosity variability was attributed to inconsistent preform consolidation.

• Residual volatile measurements on neat resin, premix, prepreg and panels presented a consistent agreement with predictive volatile levels starting with the neat resin and progressively staging the resin through a cure cycle.

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RECOMMENDATIONS

- Test methodology to measure carbon balloon intrudeability is lacking and should be addressed with an extended sink/float fluid assessment program.

- A heat treatment study is needed to assess the effect of final heat treatment temperature on carbon balloon properties, composite properties and composite performance.

- Test methodology must be developed to measure and evaluate processing effects on carbon balloon particle size distribution.

- The significance of carbon balloon size distribution on composite properties and performance should be investigated.

- Utilize Karl Fischer analysis to measure composite residual volatile levels and effusion rates. Evaluate the potential of Karl Fischer analysis data for use as a performance related acceptance test.

PERFORMANCE RELATED ACCEPTANCE TESTING

Carbon Sulfur Study

Presented to the
12th Biannual IAC Meeting
Mississippi State University
Starkville, Mississippi
May 19, 1994

Tony Day
Thiokol HSO

Pat Pinoli
Lockheed R&DD

Sulfur Analysis

During investigation of the applicability of Thermo-Jarrel-Ash Multi-Element Inductively Coupled Plasma (ICP) analytical technique to fingerprint carbon phenolic and phenolic resin -

Samples analyzed were:

1. Cured neat SC1008 phenolic resin

2. MX-4926 prepreg

3. S/N 111 AEC Fwd tag end

DC Arc Spectrography of S/N 111 Fwd tag end showed Sulfur levels at 120X background. This indicated the need for additional analysis.

The following elements were scanned and semi-quantified:

Silver, Aluminum, Boron, Barium, Calcium, Cadmium, Cobalt, Chromium, Copper, Iron, Potassium, Lithium, Magnesium, Manganese, Molybdenum, Sodium (2 wavelengths), Nickel, Phosphorous, Lead, Silicon, Tin, Titanium, Vanadium, Zinc, Zirconium (2 wavelengths).

Sulfur was indicated at 120X background, but cannot be quantified at all due to:

1. Wavelength interference from the matrix. S is quantified at 180.75 nm or 182nm. The carbon from the specimens causes interference due to the cyanogen reaction. (C + N ===> CN in the electric arc of the spectrograph)

2. Mass of the vaporized specimen is not known.

3. Multi-Element Simultaneous ICP performed for accurate quantitation.

Sulfur Analysis

Simultaneous Multi-Element Inductively Coupled Plasma Results
Thermo-Jarrel-Ash Results

Element Analyzed

Specimen

	Li	Be	Na	Mg	Al	K	Ca	V	Cr
SC-1008 Resin	BDL	BDL	BDL	0.07	BDL	BDL	BDL	BDL	BDL
S/N 111 AEC	BDL	BDL	3.6	0.9	2.0	BDL	2.9	BDL	BDL

	Mn	Fe	Co	Ni	Cu	Zn	Sr	Cd	Ba	Pb
SC-1008 Resin	BDL	0.25	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S/N 111 AEC	BDL	0.56	BDL	BDL	BDL	0.75	BDL	BDL	BDL	BDL

Note the differences between DC Arc Spectrograph Results and ICP. Many elements detected at substantial levels on DC Arc are below detectable levels on ICP for the S/N 114 specimen. The ICP is substantially more accurate than the DC Arc for these specimens.

Units are parts per million (ppm).

Sulfur Analysis
DC Arc Spectrograph Semi-Quantitative Results
at Thermo-Jarrel-Ash

Element Analyzed

Specimen	Ag	Al	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn
S/N 111 AEC	BDL	31	8	4	120	BDL	14	64	35	67	100	1.2	84	25
Prepreg	BDL	43	240	5	236	BDL	9.3	68	56	132	275	1.8	120	25

	Mo	Na	Ni	P	Pb	Si	Sn	Ti	V	Zn	Zr
S/N 111 AEC	11	161	BDL	15	682	594	1.5	8	25	10	BDL
Prepreg	4.8	343	183	16	767	576	2.3	11	57	80	BDL

NOTES:

1. SEMI-QUANTITATIVE RESULTS ONLY! Use only as a guide to more accurate methods.

2. "BDL" = Below Detection Limits

3. Values in parts per million.

Sulfur Analysis
Standard ICP Sulfur Analysis

Standard Inductively Coupled Plasma (ICP) was used to analyze for Sulfur due to wavelength interferences with the matrix (carbon).

SC-1008 showed no detectable Sulfur.

S/N 111 AEC showed 706.8 ppm Sulfur. Recovery factor was estimated at 50%.

Final result is 1413.6 ppm Sulfur.

Element: S   Wavelength: 100.731   Interval: 1   Window: 0.2 nm

Scan Name	Conc.		
○ B1.scan1	0.0		RESIN
□ U2.scan2	7.069	*	FiNiSHED PRODUCT (1:100)
△ S3.10PPM	10.00	*	
■ 4.			
• 5.			
■ 6.			
• 7.			
• 8.			

Slope: 233.66
Y-Int: 97.6587

Wavelength

180.608   180.855
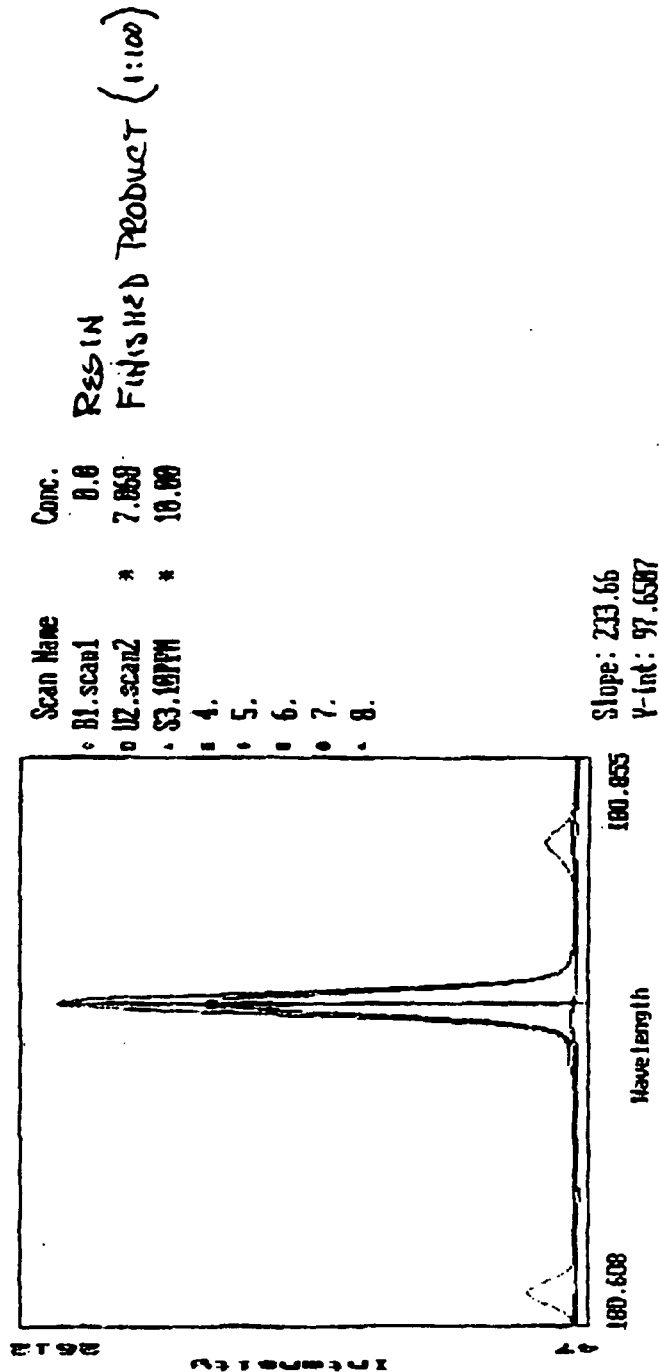
Sulfur Analysis of SC-1008 and S/N 111 AEC by Standard ICP

CARBON SULFUR STUDY

BACKGROUND

- Sulfur is a known "puffing" agent to be avoided in the manufacturing of polycrystalline graphite and C/C

- "Puffing" is characterized as a sudden irreversible expansion

    - Attributed to the release of H_2S gas

    - Occurs between 1400 - 1800 °C (> 800 °C)

    - Sulfur promotes graphitization and char yield

    - Can be inhibited with Fe_2O_3

    - Puffing action is heating rate sensitive
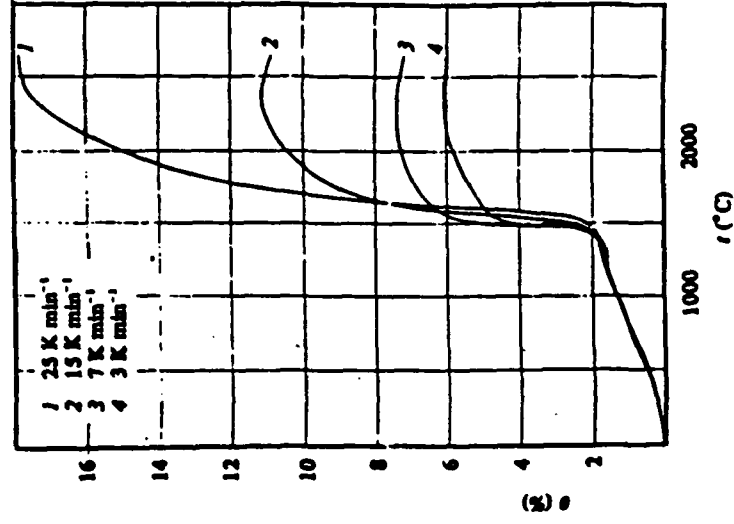
Fig. 1:

Influence of heating rate
on "puffing" according
Letizia 1977 (2)

SAMPLES SUBMITTED TO LECO FOR S ANALYSIS

- 2 rayon based carbon fiber representing RSRM grade fabrics (CCA3 and CSA)

- 1 rayon based carbon fiber representing an underfired condition (Polycarbon 10B)

- 1 rayon based carbon fiber representing an overfired condition (CCA12)

- 2 low fired PAN fiber representing Hercules LF-2 and Amoco T350/25XAB

- 1 specimen of MX-4926 prepreg tape

- 1 specimen machined from S/N 111 AEC/aft end

- 1 specimen of Type "A" carbon balloons

- 1 specimen of Type "T" carbon balloons

- 1 specimen of Shawinigan carbon black filler

Sulfur Analysis of Constituent and Composite Specimens

	Specimen	Sulfur, ppm
1.	CCA3 (Lot 36209)	1,700; 1,680
2.	CSA (Roll 7577)	1,940; 1,970
3.	Experimental Fabric 10B	1,690; 1,760
4.	CCA 12	1,840; 1,870
5.	Low Fired PAN (Hercules)	20; 60
6.	Low Fired PAN (Amoco 25)	70; 80
7.	MX-4926 Prepreg	1,680
8.	AEC S/N 111	1,890; 1830
9.	Type A Carbon Balloons	410; 410
10.	Type T Carbon Balloons	540; 560
11.	Carbon Black Filler	30; 50; 80; 100; 110

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SPECIFICATIONS FOR CARBONIZIBLE/GRAPHITIZIBLE VISCOSE RAYON YARN

	1650/720	1100/490
ASH CONTENT, %	0.45 MAX.	0.45 MAX.
SULFUR CONTENT, %	0.25 MAX.	0.25 MAX.
ZINC CONTENT, %	0.07 MAX.	0.07 MAX.
pH	5.0 - 8.0	5.0 - 8.0
FINISH EXTRACTABLES, %	0.2 - 1.0	0.2 - 1.0
TWIST PER INCH	1.6 - 2.4	1.4 - 2.2
BREAK STRENGTH, LBS.	10.3 - 13.5	7.0 - 9.6
ELONGATION, %	5.5 - 9.5	5.4 - 9.4
MOISTURE CONTENT, w%	13.0 MAX.	13.0 MAX.
DENIER, GMS/9000 METERS	1590 - 1710	1060 - 1140
SHRINKAGE, %	2.9 - 4.7	2.6 - 4.6

Total Rayon S to Carbon Conversion

Sulfur Level in Rayon	Carbon Yield Factor, w%/ppm		
	20 %	22.5 %	25 %
0.10 w%	0.50/5,000	0.45/4,500	0.40/4,000
0.20 w%	1.00/10,000	0.90/9,000	0.80/8,000
0.25 w%	1.25/12,500	1.125/11,250	1.00/10,000

PRIMARY VISCOSE REACTIONS

Steeping:

$$R_{cell}\,OH + Na\,OH \rightarrow R_{cell}\,O\text{-}Na + H_2O$$

Xanthation:

$$R_{cell}\,O\,Na + CS_2 \rightarrow R_{cell}\,O\overset{S}{\underset{\|}{-}C}\text{-}S\text{-}Na$$
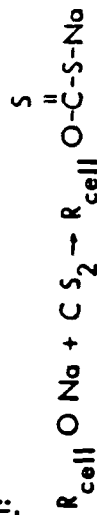
Coagulation-Regeneration

$$R_{cell}\,O\overset{S}{\underset{\|}{-}C}\text{-}S\text{-}Na + H_2SO_4 \rightarrow 2\,R_{cell}\,O\overset{S}{\underset{\|}{-}C}\text{-}S\text{-}H + Na_2\,SO_4$$

$$R_{cell}\,\text{-}O\overset{S}{\underset{\|}{-}C}\text{-}S\text{-}H \rightarrow R_{cell}\,\text{-}O\text{-}H + CS_2$$
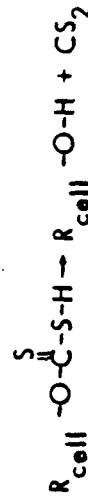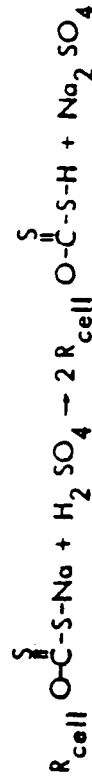
Coagulation Retardation

$$2\,R_{cell}\,O\,C\,SS \xrightarrow{\;Zn^2\;} (R_{cell}\,O\,C\,SS)_2\,Zn$$
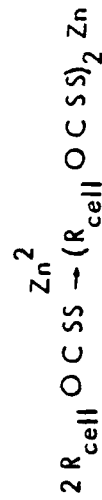
Reacted Sulfur in Rayon

- Na SO$_4$
- Zn SO$_4$
- Na Xanthate
- Zn Xanthate

Current Test Method for Measuring S in Rayon

- Liquid chemistry

- Ba sulfate precipitate

  - Proposes to measure sulfate and free sulfur

  - Nitric acid / HCl

  - Barium chloride

  - Burn off @ 800 °C for 30 minutes

CARBON SULFUR STUDY

Rayon Specification Issues

- Does the current procedure provide an accurate measurement of total S?

  - Remove skein of rayon from 5 spools being tested @ NAR for routine S analysis (Looney)

  - Submit to Leco for S analysis (Pinoli)

- Caution - dry weight vs. conditioned weight

PCI Quality System Review

1. Quality System Comparison

2. PCI Total Quality Accomplishments

    2.1   Education
    2.2   Project Teams

3. TQM

4. Modern Measures

5. Management Leadership

6. ISO9000 Certification

7. SPC Advancements

8. Strategic SPC Plan

SGL
CARBON
/ CARBON, INC ●
., 1994

MANAGEMENT LEADERSHIP

SENIOR MANAGEMENT BEHAVIOR ESTABLISHES THE TQM CULTURE

SENIOR MANAGEMENT MUST BE COMMITTED AND INVOLVED

POLYCARBON'S SENIOR MA... .... CONSTANTLY DEMONSTRATES THEIR COMMITMENT AND INVOLVEMENT BY:

- ACTIVE PARTICIPATION IN TQM PROJECT TEAMS

- COMMITMENT OF NECESSARY RESOURCES

- QUALITY IMPROVEMENTS ALWAYS DISCUSSED AT STAFF MEETINGS

- MONTHLY REVIEWS OF QUALITY PERFORMANCE

- FORMAL QUARTERLY QUALITY SYSTEM MANAGEMENT REVIEWS

TOTAL QUALITY MANAGEMENT

TQM SAYS <u>YES</u> TO ALL TRADITIONAL QUALITY ELEMENTS, BUT ADDS A WHOLE NEW DIMENSION TO QUALITY CONCEPTS.

- **DEDICATED EMPHASIS ON CUSTOMER SATISFACTION**

  - FULLY MEET ALL CUSTOMER WANTS AND NEEDS - NOT JUST SPECS.

- **CONTINUOUS IMPROVEMENT OF ALL PROCESSES**

  - EVERY COMPANY FUNCTION - NOT JUST THOSE THAT DIRECTLY AFFECT PRODUCT

- **TOTAL INVOLVEMENT OF ALL EMPLOYEES**

  - USE TEAM APPROACHES TO OPEN COMMUNICATION

- **EXPAND PERFORMANCE MEASUREMENT TO ALL PROCESSES**

  - USE STATISTICS TO MEASURE STATUS AND IMPROVEMENTS

- **FOCUS NOT ONLY ON REDUCING PRODUCT DEFECTS**

  - BUT ON REDUCING COSTS, IMPROVING SCHEDULES AND INCREASE PRODUCT PERFORMANCE

POLYCARBON TQM ACCOMPLISHMENTS

● EDUCATION

- TQM CLASSES FOR ALL EMPLOYEES
- SPECIAL CLASSES IN TQM FOR SUPERVISORS
- JUST-IN-TIME TRAINING IN TQM TOOLS AND TECHNIQUES

● SUCCESSFULLY COMPLETED TQM PROJECT TEAMS

1. RIGID FELT PRODUCTION
2. SALES INTERFACE & COMMUNICATION WITH PRODUCTION CONTROL
3. IMPROVE ACCOUNTS PAYABLE PROCESS
4. REDUCE FOIL INVENTORY
5. SPEED UP DELIVERABLE DATA PROCESS
6. IMPROVE MAINTENANCE OF FABRIC PRODUCTION EQUIPMENT
7. CONVERSION TO NEW SPINNING EQUIPMENT
8. SPEED UP FOIL MATERIAL ASSIGNMENT
9. IMPROVE COMMUNICATION BETWEEN PRODUCTION CONTROL AND QC LAB
10. IMPROVE SHIPPING AREA ENVIRONMENT
11. ESTABLISH VISUAL DEFECTS CRITERIA FOR FOIL PRODUCTS
12. IMPROVE RECEIVING DEPARTMENT PROCESSES
13. REDUCE NON CONFORMANCES IN AQ FOIL

● CURRENTLY ACTIVE TQM PROJECT TEAMS

14. REDUCE YARN COATING VARIABILITY
15. INCREASE SPC APPLICATION TO FABRIC PRODUCTION
16. REDUCE SCRAP IN FOIL PRODUCTION

MODERN MEASURES OF QUALITY

THE US BALDRIDGE AWARD

SENIOR MANAGEMENT LEADERSHIP

INFORMATION AND ANALYSIS

STRATEGIC QUALITY PLANNING

DEVELOPMENT & MANAGEMENT OF HUMAN RESOURCES

MANAGEMENT OF PROCESS QUALITY

QUALITY AND OPERATIONAL RESULTS

CUSTOMER FOCUS AND SATISFACTION

THE JAPAN DEMING PRIZE

POLICIES AND OBJECTIVES

ORGANIZATION

EDUCATION

INFORMATION FLOW

PRODUCTS AND PROCESS QUALITY

STANDARDIZATION

CONTROLS AND MANAGEMENT

Q. A. FUNCTIONS

RESULTS

STRATEGIC PLANS

QUALITY SYSTEM COMPARISON

TRADITIONAL QUALITY ELEMENTS	SECTION OF MIL STD 9858A	SECTION OF ISO 9000
MANAGEMENT RESPONSIBILITY	3.1	1
QUALITY SYSTEM	3.3	2
CONTRACT REVIEW	3.2	3
DESIGN CONTROL	4.1	5
DOCUMENT CONTROL	4.1	5
PURCHASING	5.1, 5.2, 7.2	6, 7
IDENTIFICATION AND TRACEABILITY	6.1	8
PROCESS CONTROL	6.2	9
INSPECTION AND TESTING	6.1, 6.3, 6.7, 7.1	10, 12
TEST EQUIPMENT	4.2 - 4.5	11
NON CONFORMING PRODUCT	6.5	13
CORRECTIVE ACTION	3.5	14
HANDLING/PACKAGING/DELIVERY	6.4	15
RECORDS	3.4	16
SPC	6.6	20
INTERNAL AUDITS	-	17
TRAINING	-	18
SERVICING	-	19
QUALITY COSTS	3.6	

ISO 9000 IS A STRICT INTERPRETATION OF 9858A BASICS

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POLYCARBON, Inc. ●
April, 1994

PROGRESS TOWARDS ISO 9000 CERTIFICATION

MAJOR STEPS	STATUS
1. DEVELOP NEW QUALITY MANUAL	COMPLETE
2. DEVELOP 20 NEW HIGH LEVEL QUALITY PROCEDURES	COMPLETE
3. SELECT AND SIGN-UP WITH REGISTRAR	COMPLETE
4. REGISTRAR REVIEW/ASSESSMENT OF QUALITY MANUAL AND PROCEDURES	COMPLETE
5. DEVELOP OVER 200 NEW OR REVISED DETAILED PROCEDURES	COMPLETE
6. REVIEW AND RELEASE OVER 400 NEW OR REVISED FORMS	JUNE 94
7. FINAL REVIEW AND UPDATE OF ALL DOCUMENTATION	JUNE 94
8. REGISTRAR FINAL ASSESSMENT OF QUALITY DOCUMENTS	JULY 94
9. COMPLETE TRAINING AND QUALIFICATION REQUIREMENTS	SEPT 94
10. ON SITE ISO 9002 AUDIT	OCT 94
11. CORRECT FINDINGS (IF ANY)	NOV 94
12. OBTAIN CERTIFICATION	NOV 94

III. SPC ADVANCEMENTS

- Secured a full time dedicated SPC Coordinator

- Developed SPC training and implementation plans

- SPC training Accomplishments

  - SPC handbook
  - Basic SPC classes for all employees
  - SPC charting classes for operators

- Special SPC training by an outside ASQC Consultant

  - Design of experiments
  - Statistics for Quality and Engineering
  - Statistical process control for Production

III. SPC ADVANCEMENTS (Con't)

- Control charts being applied to our processes

  - 12 control charts have now been implemented in the company including:

    - Foil thickness
    - Yarn furnace temperature
    - Fabric furnace temperature
    - Salt particle size distribution
    - Fabric visual defects after scouring

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SPC PLAN

1.0 OBJECTIVE

1.1 Identification:
- select all potential Quality characteristics and parameters.
- a joint effort of both PCI and customer involvement.
- priontizing the critical choices to be identified and analyzed.
- assign the appropriate equipment and instruments.
- determine if the vanation is measurable.

1.2 Implementation:
- provide comprehensive training to all personnel whose duties directly affect the quality of the product.
- training in the basic statistical techniques used in the facility, referencing the SPC Handbook P-005.
- collect data on the critical characteristics to develop a statistical history.
- control charts will be selected to indicate the changes in the process when they occur.

1.3 Analysis:
- deductive reasoning in all Out of Control Conditions to determine the cause of this condition.
- assign a conclusion (cause) to the condition.
- label it directly on the control chart.
- Continue to plot and analyze the chart.
- analyze the data collected by using the capability study.
- develop a standard from the data, Statistical Tolerancing.

1.4 Improvement:
- determine a plan of action based on the results.
- modify the methods and implement the appropriate changes on the process.
- The cycle continues in determining if the characteristic was significant.
- evaluate the changes affected the process.
- improve the quality of the product.
- Determine if further analysis is needed.

2.0 ORGANIZATION

Statistical Process Control Coordinator- J. Yang

- SPC training to all employees in the facility
- Assist in the selection of Quality Characteristics.
- Organize the implementation of control charts
- Develop Statistical Process Control plans/schedules
- Provide Statistical Analysis for Special Projects
- Be a statistical resource for engineering and production in SPC. Capability, Gage R&R and DOE.

Statistical Process Control Specialist- P. Lainez

- SPC training to all employees in the facility- Spanish speaking
- Assist in the selection of Quality Characteristics
- Organize the implementation of control charts
- Provide support for Spanish speaking employees
- Be a statistical resource for engineering and production in SPC, Capability, Gage R&R and DOE

The selection of the appropriate control chart will be in a team approach, with the SPC Coordinator/Specialist as a guide. Control charts are the responsibility of each individual operator with the support of their supervisor. SPC Coordinator/Specialist are resources to assist the operator in better understanding the charts and the interpretation of "out of control conditions".

3.0 EDUCATION

- PCI Handbook P-005
- Introduction to SQC Course
- Introduction to SQC Course in Spanish
- Develop training guideline for the SQC Course
- Introduction to Metrology
- Advance SPC Course
- Design of Experiments
- Statistics for Quality Engineers

4.0 MAJOR TASKS

- Introduce all employees to the concepts of Statistical Quality Control.
- Just in Time training to those employees who have immediate needs for the control chart
- Implement control charts and properly use the indications of "out of control conditions".
- Educate all employees in the results of these conditions and provide appropriate controls to the system
- Assure continuous process improvement throughout the company

5.0 TASK ASSIGNMENTS

Control Charts are being implemented throughout the facility. Presently, implemented control charts are being carried out on quality characteristic and process parameters. All Supervisors will be given the responsibility, a minimum, of one control chart in their department. As the supervisors become more proficient with the control chart, operators will be introduced to these concepts of indicating "out of control conditions" in the process.

	Characteristic	Product	Location	Chart	Responsible	Ident	Implem	Analyze	Improve
1	Thickness - N	Foil	Master Roll	X/R (u)	D.Kershaw	X	X		
2	Thickness - S	Foil	Master Roll	X/R (u)	D.Kershaw	X	X		
3	% Mixture	Foil	Master Roll	TBD	D.Kershaw	X			
4	Area Weight	Foil	Master Roll	IMR	J.Morales	X	X	X	
5	Part. Size, Dist	Foil	Sifter	Chi Sqrd	J.Taylor	X	X	X	X
6	Calibration	QC Lab	Orion IonA	X/R	J.Taylor	X	X	X	X
7	Yarn Weight	Yarn	Braided Foil	Xbar/R	J.Miranda	X	X		
8	Finish Content	Yarn	Braided Foil	Xbar/R	J.Miranda	X	X		
9	Furnace Temp	Yarn	Yarn Lindy	X/R (u)	J.Miranda	X	X	X	
10	Visual Defects	Fabric	Rimer	C	R.Jimenez	X	X	X	
11	Visual Defects	Fabric	Master Roll	P	R.Jimenez	X	X	X	
12	Furnace Temp	Fabric	Master Roll	X/R	R.Jimenez	X	X		
13	TBD	Felt	Production	TBD	A.Salus	X			
14	Visual % Defect	Foil	Rewinder	P	F.Zumora	X			
15	Completed SWO	Service	Prod Control	TBD	S.Anderson	X			
16	TBD	Service	Accounting	TBD	BJ.Schramm				
17	TBD	Service	Cust. Service	TBD	F.Cole				
18	Cert. Defects	Service	Doc. Control	TBD	L.Robinson	X			
19	Conductivity	Service	Furnace Water	X/R	D.Buro	X	X		
20	pH	Service	Furnace Water	X/R	D.Buro	X	X		
21	TBD	Service	Shipping	TBD	T.Palacios				

* Deviation From Target Control Charts

Engineering will be given the task of applying Capability studies to new and existing processes and Designing of Experiments to provide an efficient means of understanding the process parameters and its interactions.

Prepared By: _Jerry Yang_   SPC Coordinator   Date: _3 May 99_

Approved By: _Dave Beaumont_ - Quality Manager   Date: _3 May 99_

Statistical Quality Control

ID	Name	Duration	Scheduled Start	Scheduled Finish	Critical	% Complete
1	Development	128d	6/28/93 8:00am	12/23/93 5:00pm	No	100%
2	PCI Handbook P-005	40d	6/28/93 8:00am	8/20/93 5:00pm	No	100%
3	Training Guidelines	21d	8/6/93 8:00am	9/3/93 5:00pm	No	100%
4	Translate P-005 to Spanish	44d	10/18/93 8:00am	12/17/93 5:00pm	No	100%
5	Guidelines - translated	28d	11/15/93 8:00am	12/23/93 5:00pm	No	100%
6	Company Training	234.25d	9/13/93 8:00am	8/8/94 10:00am	Yes	51%
7	SQC Training	143.44d	9/13/93 8:00am	4/1/94 11:30am	No	88%
8	QC Laboratory	1h	9/13/93 8:00am	9/13/93 9:00am	No	100%
9	QC Inspection	1h	9/24/93 8:00am	9/24/93 9:00am	No	100%
10	Prod. Supervisors	2h	10/13/93 8:00am	10/13/93 10:00am	No	100%
11	Sales/Cust. Service	2h	11/8/93 8:00am	11/8/93 10:00am	No	100%
12	Accounting	2h	2/17/94 10:00am	2/17/94 12:00pm	No	100%
13	Engineering	2h	3/4/94 9:30am	3/4/94 11:30am	No	100%
14	Maintenance	2h	3/14/94 3:00pm	3/14/94 5:00pm	Yes	0%
15	Prod Control	2h	3/25/94 9:00am	3/25/94 11:00am	No	100%
16	Doc Control	2h	4/1/94 9:30am	4/1/94 11:30am	No	100%
17	SQC Training - Spanish	86.5d	4/7/94 3:00pm	8/8/94 10:00am	Yes	3%
18	Fabric	2h	4/7/94 3:00pm	4/7/94 5:00pm	No	15%
19	Yarn	2h	5/7/94 8:00am	5/9/94 10:00am	Yes	0%
20	Foil Line	2h	6/6/94 8:00am	6/6/94 10:00am	Yes	0%
21	Cal Carbon	2h	7/4/94 8:00am	7/4/94 10:00am	Yes	0%
22	Felt	2h	8/8/94 8:00am	8/8/94 10:00am	Yes	0%
23	Control Chart Course	137.75d	12/29/93 2:00pm	7/11/94 11:00am	No	39%
24	Foil Line	3h	12/29/93 2:00pm	12/29/93 5:00pm	No	100%
25	Cal Carbon	3h	2/28/94 2:00pm	2/28/94 5:00pm	No	100%
26	Yarn	3h	3/3/94 2:00pm	3/3/94 5:00pm	No	100%
27	Fabric	3h	3/25/94 2:00pm	3/25/94 5:00pm	No	100%
28	Felt	3h	4/11/94 2:00pm	4/11/94 5:00pm	Yes	0%
29	Maintenance	3h	4/25/94 8:00am	4/25/94 11:00am	No	25%
30	Cust Service	3h	5/9/94 8:00am	5/9/94 11:00am	Yes	0%
31	Accounting	3h	5/23/94 8:00am	5/23/94 11:00am	Yes	0%
32	Shipping	3h	6/6/94 8:00am	6/6/94 11:00am	Yes	0%
33	Prod Control	3h	6/20/94 8:00am	6/20/94 11:00am	Yes	0%
34	Doc Control	3h	7/11/94 8:00am	7/11/94 11:00am	Yes	0%
35	Design of Experiment	3d	9/27/93 8:00am	9/29/93 5:00pm	No	100%
36	Advance SPC Course	6d	11/29/93 8:00am	12/7/93 5:00pm	No	100%
37	Statistic for Quality Engineering	2d	12/8/93 8:00am	12/9/93 5:00pm	No	100%

Page 1

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Statistical Process Control Plan For Fabric
1994

	Description	Chart Type	Date Planned
1.1	**Rimar**		
	• Incoming Fabric Visual Defects	P	retraining
1.2	**Fabric Ovens**		
	• Ovens A through E Temperature	Pareto	August 94
1.3	**Fabric Furnace**		
	• Furnace Temperature	X̄/mR	Implemented
	• Dryer Temperature	X̄/mR	July 94
1.4	**Fabric Wash Water**		
	• Wash Water pH	X̄/mR	Implemented
	• Wash Water Sodium	X̄/mR	June 94
	• Wash Water Conductivity	X̄/mR	Implemented
1.5	**Master Roll Inspection**		
	• Master Roll Visual Defects	P	May 94

HIGHLAND (AB) FABRIC DEFECT

APRIL 1994

TYPE OF DEFECT	NUMBER OF DEFECTIVE YARDS FOUND	% DEFECTIVE YARDS PRE TOTAL DEFECTIVE YARDS FOUND	%DEFECTIVE YARDS PRE TOTAL YARDS SCOURED
Pulled Threads	129	54.89	0.84
Fuzzy	53	22.55	0.35
Soots	17	7.23	0.11
Weave	29	12.34	0.19
Wrinkle	4	1.70	0.03
Holes/Tears	0	0.00	0.00
Folds	0	0.00	0.00
Splices	0	0.00	0.00
Other*	3	1.28	0.02
Total	235	100.00	1.54

DEFECTS STATISTICS

of rolls scoured = 70

# of yards scoured = 15279

% Defective per total yards = 1.54

Average # of defective yards per roll, $x = 3.4$

Upper Control Limit, $UCL_c = 30$
(calculated from historical data)

Lower Control Limit, $LCL_c = 5$
(calculated from historical data)

*Note control charts show that the "other" defects can be caused by both vendors and PCI. The number in the chart above reflect only the vendor's defects.

PARETO CHART FOR HIGHLAND(AB) FABRIC
APRIL 1994

Defective Yards = 235

Count

140
120
100
80
60
40
20
0

Pulled Threads
Fuzzy
Weave Defects.
Spots
Wrinkles
Other
Folds
Holes/Tears
Splices

Type of Defect
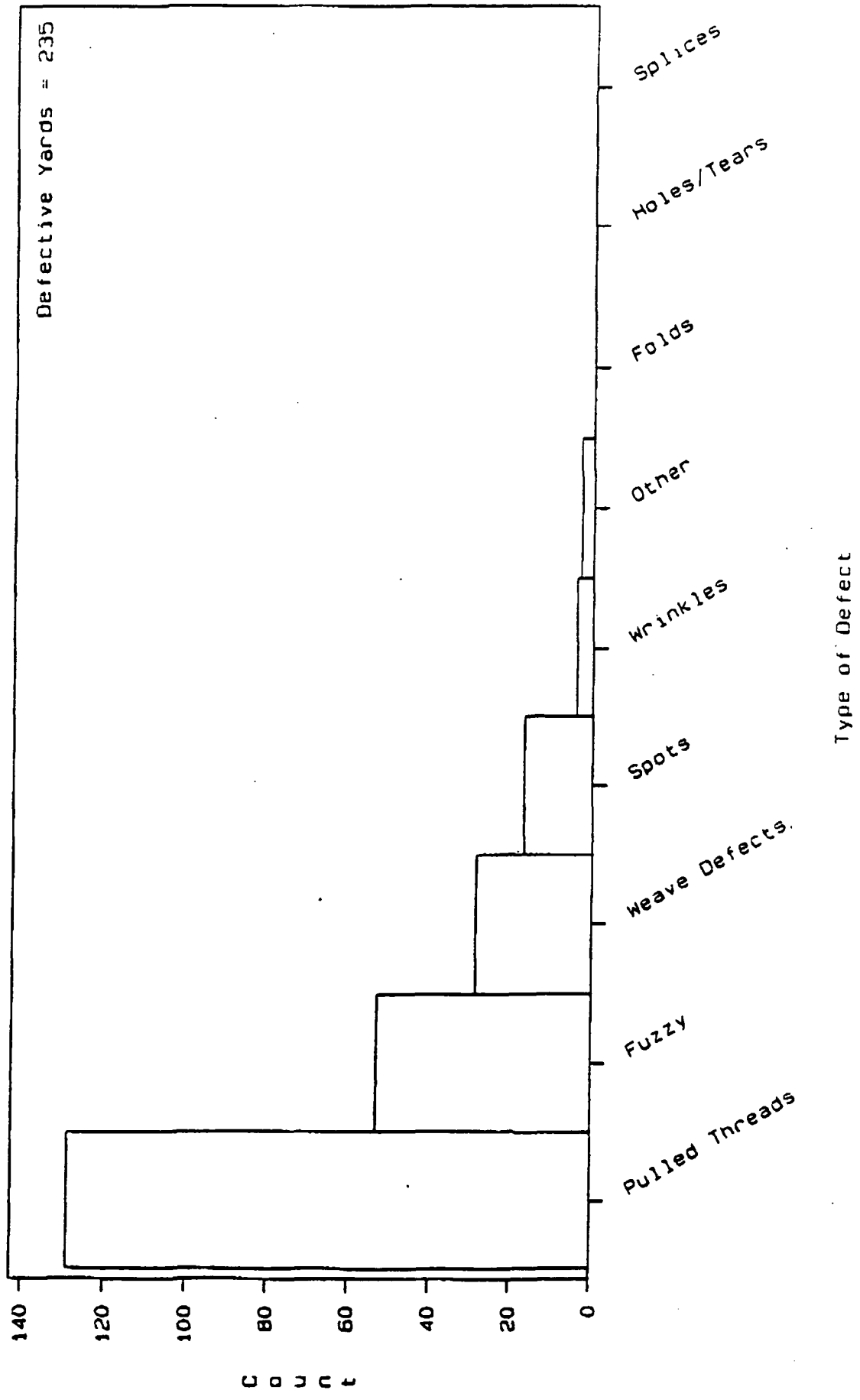
TREND OF PERCENT DEFECTIVE YARDS
PER TOTAL YARDS SCOURED
HIGHLAND (AB) FABRIC
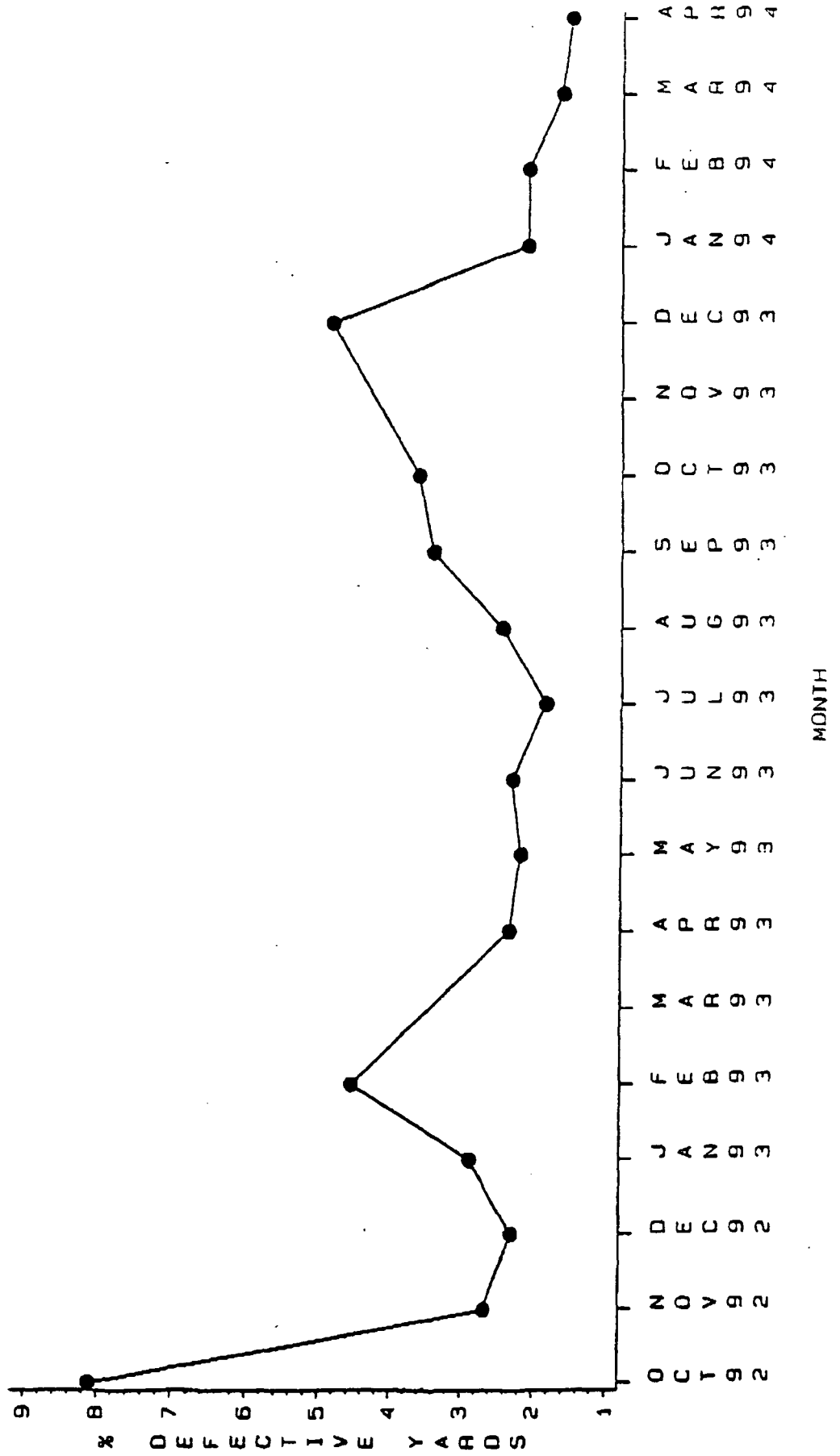
JON WEISPFENNING

SPC PROGRAM

ICI FIBERITE

PRESENTED TO SPIP SUBCOMMITTEE

FOR TEST METHODS

MAY 19, 1994

FIBERITE

A business unit of ICI Composites Inc

HISTORY

STARTED 2ND HALF 1988

SQC
RAW MATERIAL
INTERMEDIATES
SELECTED FINISHED GOODS

SUCCESSES

– KARBON 647

CONSTRAINTS

– LACK OF KNOWLEDGE

WHAT SPC IS:

– Statistical methods for analyzing and controlling the variation of the process

WHAT SPC IS NOT:

– Control charts on properties not controlled by the process

SODIUM LOT AVERAGES FOR MX 4926
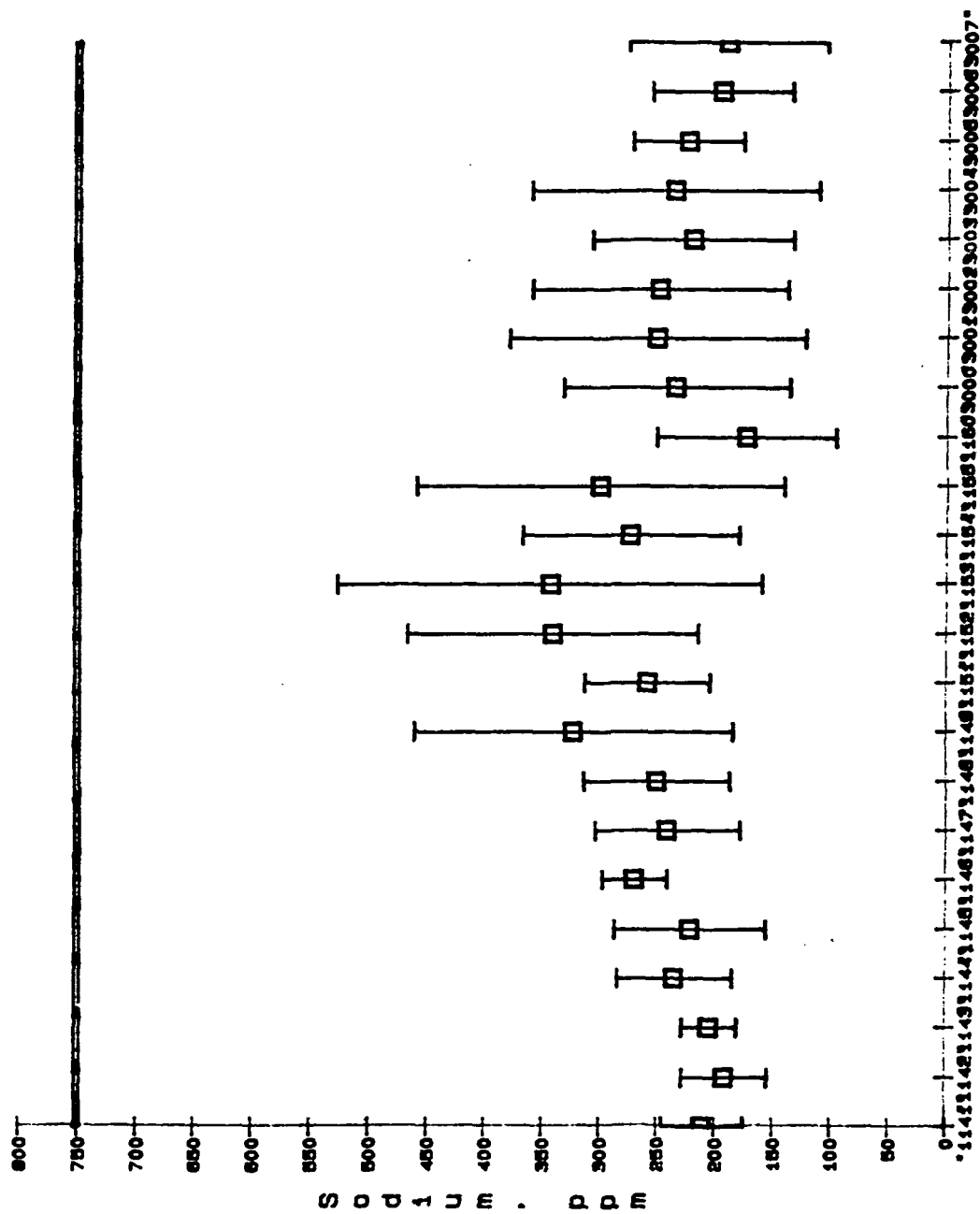
750 ppm Max USL

SODIUM LOT AVERAGES FOR MX-4926
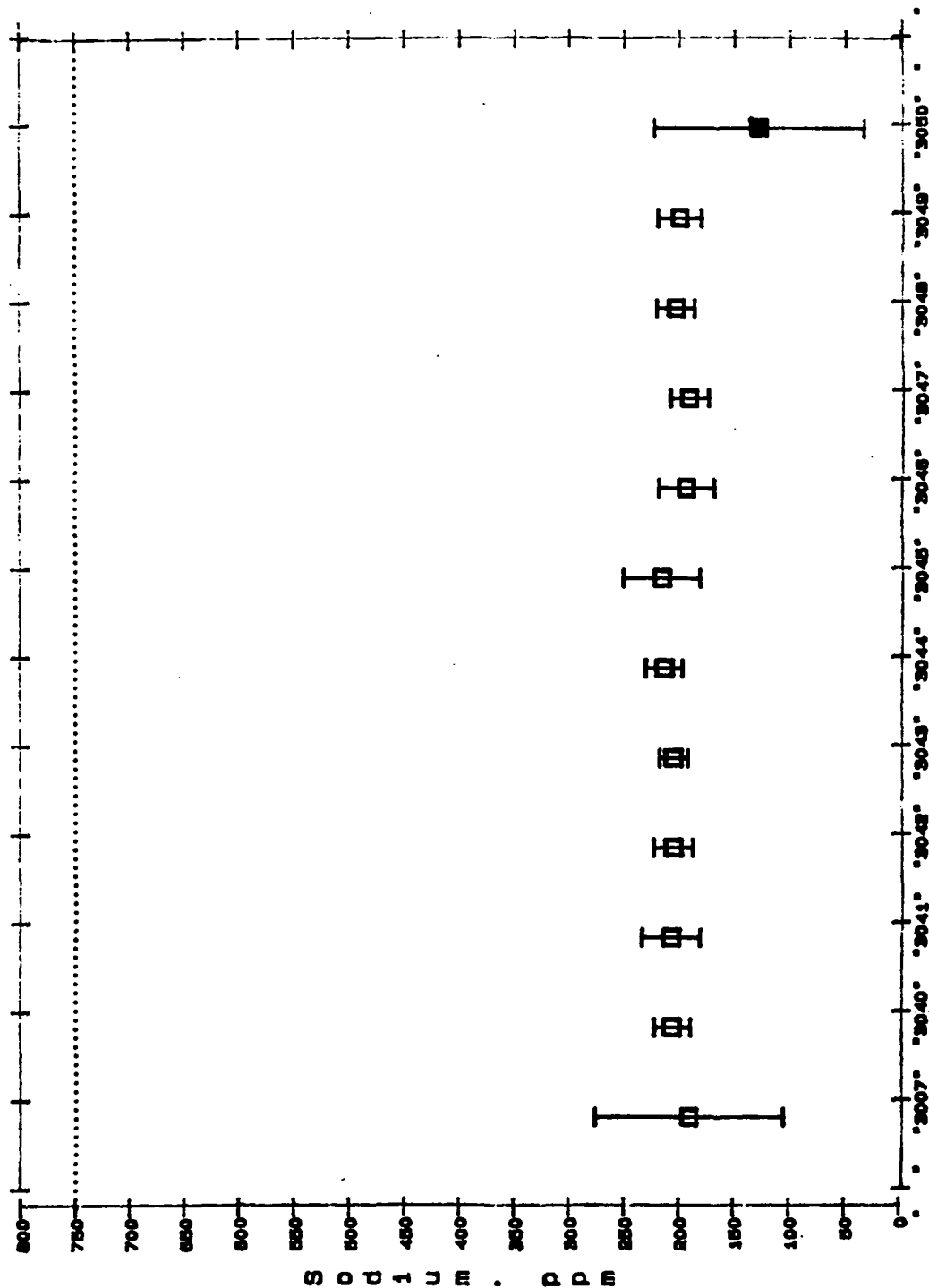
750 ppm
Max USL.

COMPRESSION STRENGTH HISTORY OF MX 4926
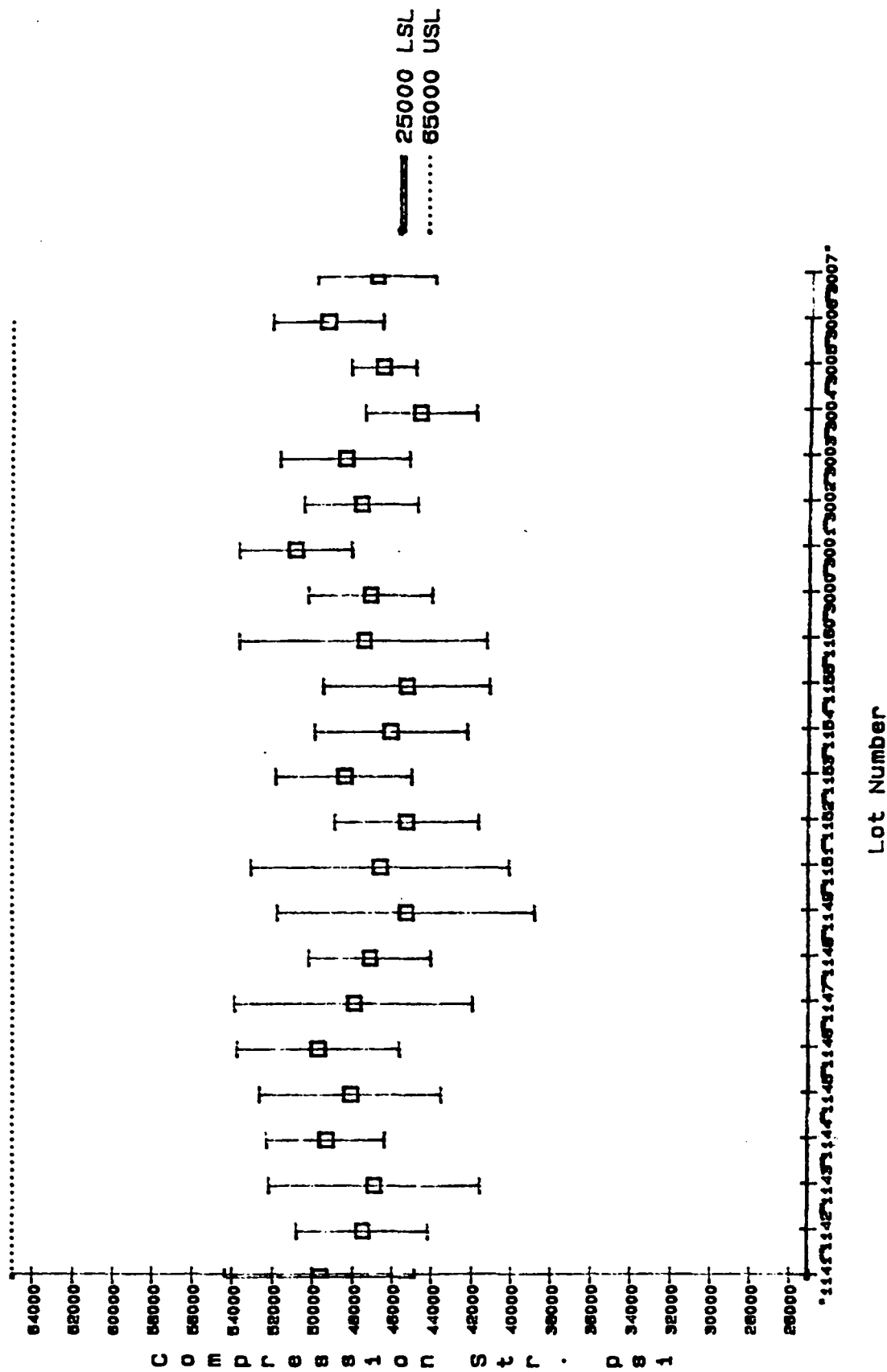
SPC

IMPLEMENTATION

GUIDE

ICI/FIBERITE
Winona, MN
February 4, 1992

X-BAR AND RANGE CONTROL CHART

Part:MX-4926-1S
Char: FLOW

Description:
Subgroups: 237   Subgroup Size: 1
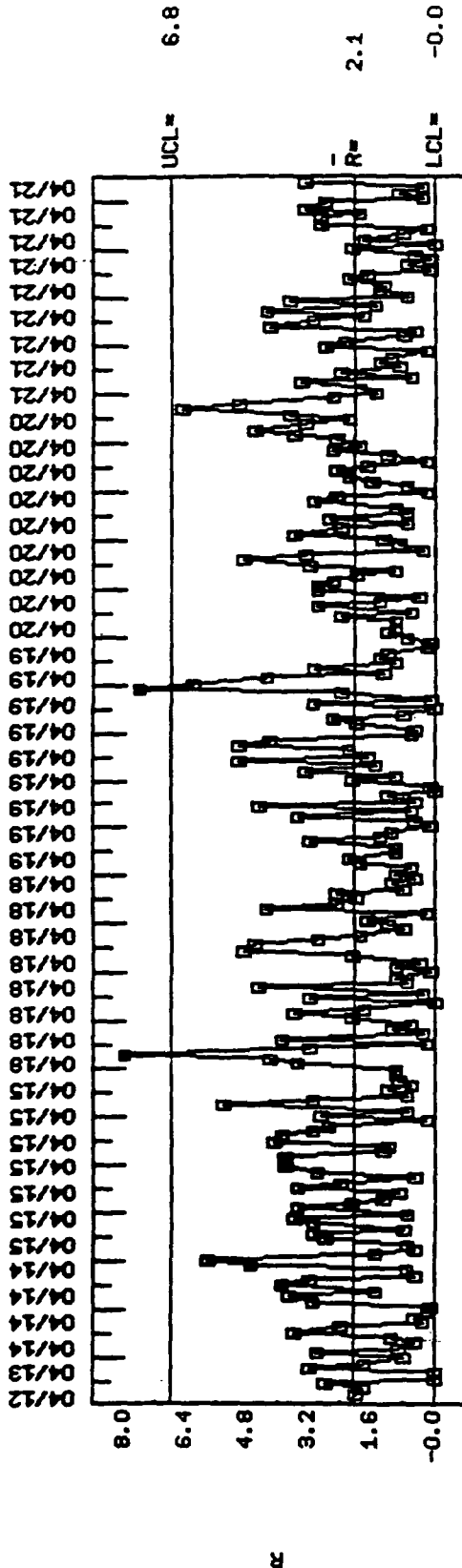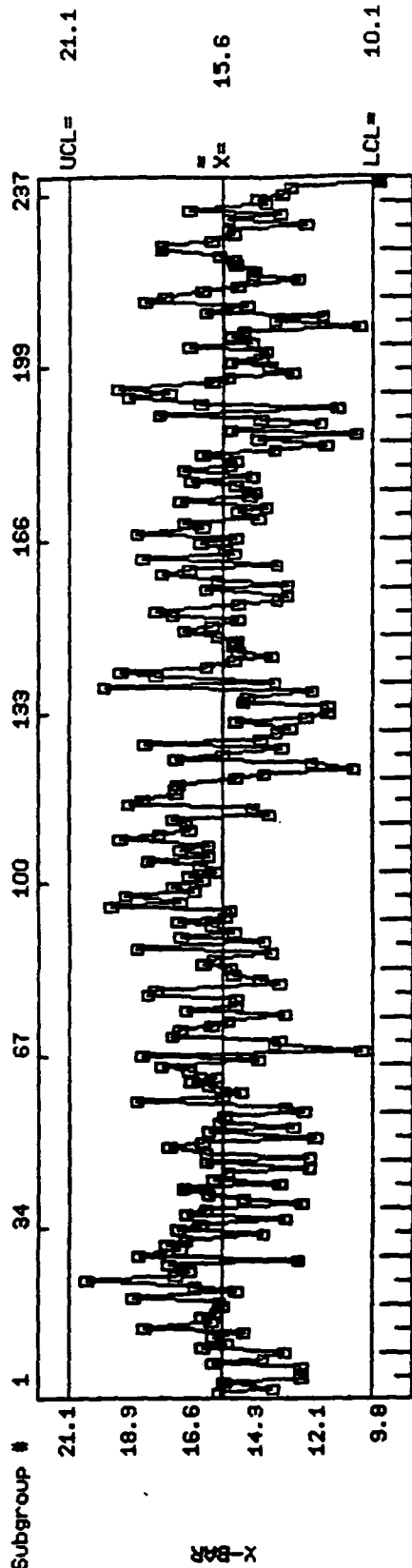
04/22/94
12:39:58

- MX-4926 SUCCESSES

- WHY MP&E

- THE MP&E GOAL

- EXAMINING THE PROCESS

- WHAT IS THE PROCESS

- HOW TO EFFECT IMPROVEMENT

ICI FIBERITE

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Percent Shipped that is Produced of MX-4926

Percent

Lot #

· Ind. —— 5 Lot Avg ···· LCL ···· UCL
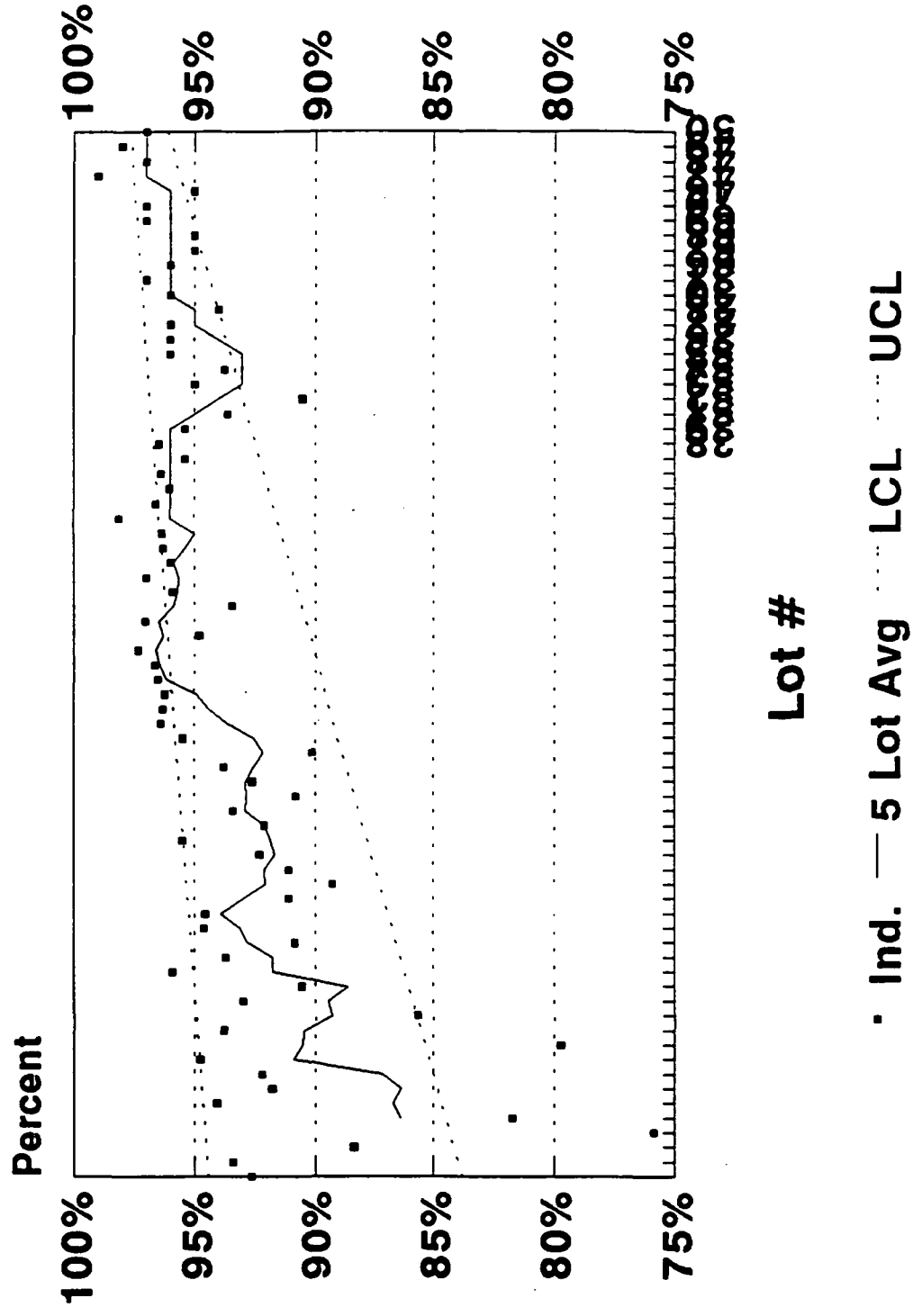
Why MP&E

- The Major problem is product variability.

- Most of this variability is caused by variability in our processes.

- This cannot usually be resolved, or even reliably detected by conventional QA/QC examination of the material.

- Therefore, focus on control of the manufacturing process and inputs, not control of the product after the event.

MP&E MISSION

REDUCE MATERIAL VARIABLILITY BY
CONTINUOUSLY IMPROVING THE CONTROL
OF THOSE PROCESS PARAMETERS TO WHICH
THE MATERIAL IS SENSITIVE AND THAT
ENSURE SATISFACTORY PERFORMANCE IN THE
CUSTOMER'S PROCESS.

THE PROCESS IS WHAT THE MATERIAL "SEES"

- Each process step is relevant if it includes exposure of the material to conditions which can effect its characteristics.

- The nominal control paramters are indirect. There is usually some translation mechanism which can:

  - Alter our perception of what is really imposed on the material.

  - Is subject to interference from other factors controlled and uncontrolled which leads to true variation even when the nominals are held constant.

- There are "forces" acting on the materials which are not controlled, or poorly controlled, by our documentation.

FIBERITE

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THE M-P-C MODEL

- Meausrement
  without it there is no means of identifying
  patterns or comparison.

- Pattern
  without we cannot assess process product
  response sensitivity.

- Comparison
  without it we cannot develop more general
  rules on the process and material
  characteristics.

HOW TO EFFECT IMPROVEMENT

- Don't try to outguess your customer

- Product variability arises mostly from process variation.

- Stabilize the process factor that are prime in changing the customer sensitive product charactristics.

- Plan-Do-Study-Act

- Need Fundamental Change

- SPC/SQC, DOE, ETC.

ICI FIBERITE

A business unit of ICI Composites Inc.

HYBOY IMPROVEMENT TEAM

HISTORY: The Hyboy Department consists of three production lines that produce FMM materials used in the aerospace. automotive, and electrical industries.

SPC: SPC charting in this department at the beginning of 1992 indicated that our scrap was averaging approximately 5%.   Production yields for the departments four major products averaged 82.4%.

PROCESS IMPROVEMENTS:

The production team which was given the task of improving our scrap and yield percentages focused their efforts on the following:

- Changing the recirculation system
- Adding more strings to the Hyboys
- Installing new bearings to the choppers
- Increasing the diameter of the "Sky Rolls"
- Changed chopper knives
- Better monitored the resin specific gravity

RESULTS: SPC charting following these improvements indicated that scrap was now averaging 1.9%. Yields of the four major products in the HyBoy Department had improved to an average of 91.3%.

This team was recently presented the Minnesota Council for Quality Award from Minnesota Governor Arne Carlson.

DEMING CYCLE	TQT PROCESS STEP	PURPOSE OF STEP	IMPROVEMENT TOOLS*
PLAN	Define System	To agree on aim, size, scope of the project and to gather data on each quality measure	Check Sheet, Flow Chart, Operational Definition, Run Chart, Sampling
	Assess Current Situation	To have knowledge of system performance	Capability Analysis, Cause & Effect Diagram, Chart Interpretation, Control Charts, Force Field Analysis, Histogram, Nominal Group Technique, Pareto Diagram, Systematic Diagram
	Analyze Causes	To have a theory for system improvement	Affinity Diagram, Cause & Effect Diagram, Chart Interpretation, Control Charts, Histogram, Nominal Group Technique, Pareto Diagram, Relations Diagram, Sampling, Scatter Diagram
DO	Try Out Improvement Theory	To test the improvement theory	Force Field Analysis, Systematic Diagram
STUDY	Study The Results	To see if the theory worked	Capability Analysis, Chart Interpretation, Control Charts, Histogram, Pareto Diagram
	Standardize Improvements	To fully implement the improvement	Chart Interpretation, Check Sheets, Control Charts, Flow Chart, Sampling, Systematic Diagram
	Plan Continuous Improvement	To have team's recommendations for continuous improvement	Affinity Diagram, Capability Analysis, Control Charts, Force Field Analysis, Histogram, Nominal Group Technique, Pareto Diagram, Relations Diagram, Systematic Diagram

*Team Skills are used throughout

CARBON-PHENOLIC ACCEPTANCE TESTING

12TH INDUSTRY ADVISORY COMMITTEE MEETING
STARKVILLE, MISS

18-19 MAY 1994

KEITH H. HILL

PRESENTLY USED ACCEPTANCE TESTING MAY NOT ADDRESS PERFORMANCE -- RESULT IS LACK OF INDUSTRY UNDERSTANDING FOR SUCCESS/FAILURE

```
Characterization
      Tests
          │
          ▼
    Design &
    Analysis
          │
          ▼
  Manufacturing
          │
          ▼
  Constituent ──No──▶ Scrap
  Acceptance
      │ Yes
      ▼
   Prepreg ──No──▶ Quick ──No──▶ Scrap
  Acceptance         Fix
      │               │ Yes
      │               ▼
      │         Tweek Process
      │◀────Yes── or Viscosity
      │ Yes
      ▼
   Part Tag ──No──▶ MRB ──Not──▶ Scrap
  Acceptance              OK
      │ Yes            │
      ▼          OK - But now what?
  Useable Material ◀────┘
      │ Yes
      ▼
  Anomaly-free ──Yes──▶ All Acceptance
  Performance              Criteria Met
      │                 
      │              ──▶ Not All Acceptance
      │                   Criteria Met
      │ No
      ├──▶ All Acceptance
      │     Criteria Met
      └──▶ Not All Acceptance
            Criteria Met
```

THE IDEAL SCENARIO

WHAT IS REQUIRED FOR ACCEPTANCE TESTS TO MEASURE PROPERTIES MEANINGFUL TO PERFORMANCE?

Characterization Testing	+	Design/Analysis	+	Manufacturing	+	Acceptance Testing

Characterization Testing

- *Properties are representative of nozzle material properties*

- Valid - Design / Analysis performance driven parameters are measured

Design/Analysis

- Models incorporate right science
  - Physics
  - Chemistry
  - Mechanics

- Design decisions based on sensitivities to variations in critical properties

- Models use valid characterization data

Manufacturing

- Constituents certified to performance driven properties / limits

- Process control ensures consistency

- Material represents what was characterized and analyzed

Acceptance Testing

- Valid - Measures performance related properties

- Reliable - Standardized for high level of confidence in precision, accuracy

- Adequate sampling

- *Correct sample preparation (test methodology)*

kth/maw/9404208.drw

CARBON-PHENOLIC ACCEPTANCE TESTING - CURRENT POSITION

- Purpose

  - Provide quick turn-around data for accept/reject criteria

  - Provide confidence to proceed/use

- Characteristics

  - Short response time - should not hold up processing

  - Inexpensive - easy sample preparation, reasonable equipment costs

  - Reliable - consistently performed for precision and accuracy

  - Validity - data should represent meaningful properties

- Result

  - Confidence that material in question represents historically successful material, i.e., consistent constituents and processing

  - Confidence that material in question will perform per design (drawing and spec)

SPIP IS SEEKING TO IMPROVE MATERIAL AND PROCESS SCIENCE

- Standardize Constituent and Acceptance Test Methods

- Improved Process Understanding and Control

- Increase Understanding of Phenolic Resin

  - As received chemistry

  - Cure kinetics

  - Viscosity

- Develop New Tests for Performance Based Acceptance of Cured Material (Tags)

  - Permeability - RT and Elevated Temperature

  - Karl Fischer

  - Other

Increased Understanding of Cured Material Behavior

- Exploratory material property testing, e.g., pore pressure phenomena, torsional shear

- Code improvement for better modeling

- Instrumentation advances

  - Pore pressure gage

  - Thermal probes

C-5.

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SOME EXAMPLES OF CURED CARBON-PHENOLIC SPEC REQUIREMENTS

ITEM	CURED MATERIAL TESTS (PREPREG)	COMPONENT TAG TESTS		
	S13037 (Delta)	S273059 (Delta)	S283081G (Titan)	WS18445B (D-5 SS)
Document				
Test Samples	Cured Flat Panel - 325 ± 10°F, 120 ± 15 min 1000 psi	From Billet	From Billet	From Billet
Cross-Ply Tensile	N/A	800 psi min	N/A	N/A
Specific Gravity	1.40 - 1.55	1.40 min	1.40 min	1.40 - 1.52
Resin Content	30 - 38.5%	30 - 40%	30 - 39%	28 - 40%
Vol Content (4 HR) Vol Content (18 HR)	2.5% max N/A	3.0% max N/A	3.0% max 3.8% max	3.5% max N/A
Flex Strength (W) Flex Strength (F)	25,000 - 55,000 20,000 - 50,000	N/A	20,000 psi min	17,000 - 43,000
Comb. Resin & Vol Content	N/A	N/A	N/A	43.0% max
Comp Strength (Edgewise) Warp	45,000 - 75,000 psi			
I/L Double Shear	3,500 - 8,000 psi			
Thermal Cold (fill) Warp Fill	.1 - 1.1 btu/hrft°F .1 - 1.1 btu/hrft°F			
CTE (75-400°F) Cross Ply With Ply	5.0 - 20.0 in/in°Fx10^{-6} 2.0 - 8.0 in/in°Fx10^{-6}			
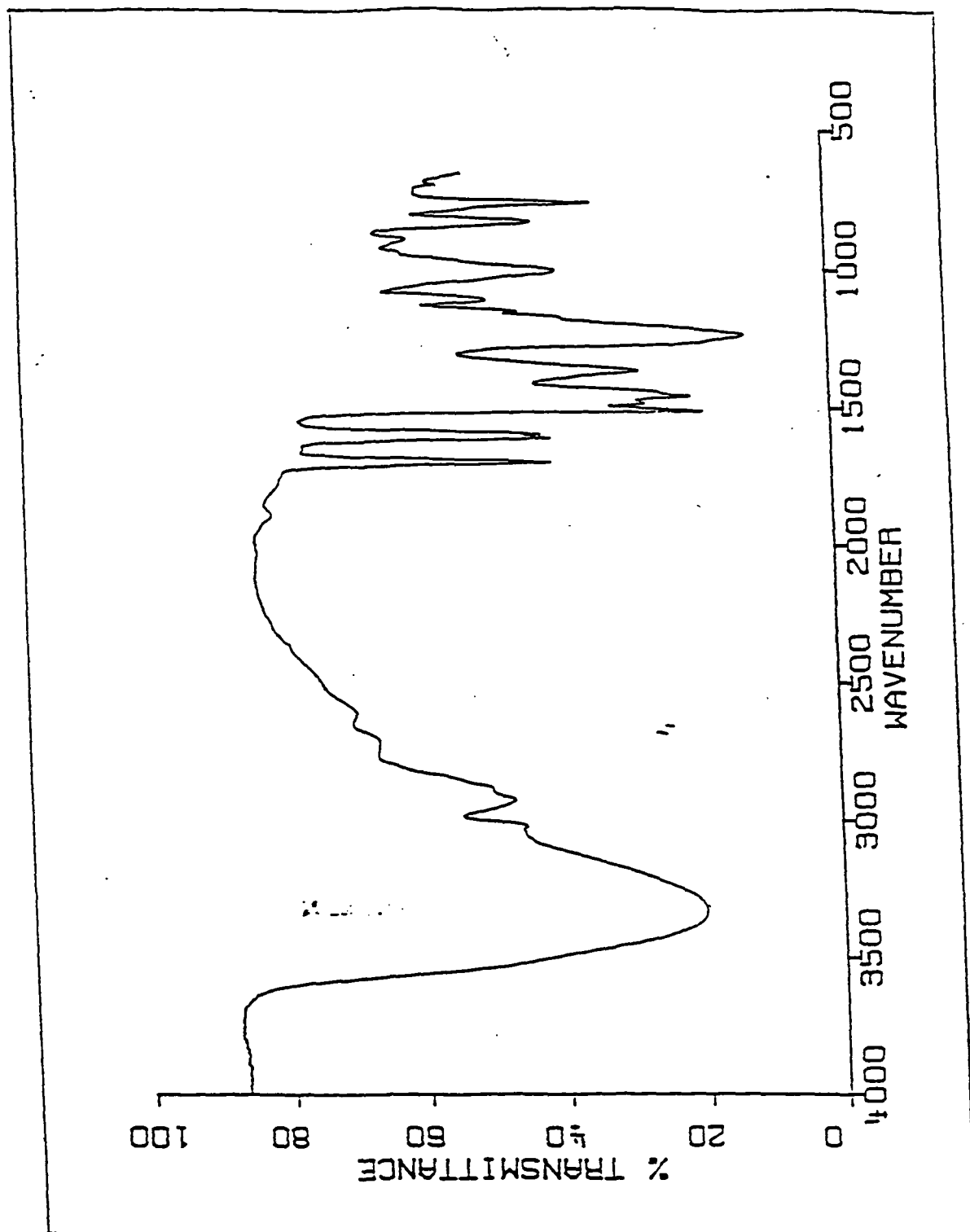
Figure 2. Infrared Identification of Resin

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(Technical society and technical association specifications and standards are generally available for reference from libraries. They are also distributed among technical groups and using federal agencies.)

3.0 REQUIREMENTS

3.1 Material. The material shall be carbon fabric reinforcement manufactured from 8-harness satin weave rayon-base fabric, and final processed at a temperature of 2,000 degrees to 2,850 degrees Fahrenheit (F). Material manufactured from rayon-base material supplied by an unqualified supplier (see 6.3) shall be identified as S13140-001.

3.2 Properties.

3.2.1 Chemical and physical properties. Chemical and physical properties of the reinforcement shall be as specified in table I.

Table I. Chemical and Physical Properties

Property		Value	
		Minimum	Maximum
Carbon assay	Percent	94.0	—
Moisture content	Percent	—	3.0
Ash Content	Percent	—	1.0
Weight	Ounces per square yard	7.0	9.5
Breaking strength	Pounds per inch width		
Warp direction		20	—
Fill direction		15	—
Specific gravity at 25°C		1.7	1.9
Thickness	Inches	0.016	0.021

3.3 Marking. Each roll of the material covered by this specification shall be marked in a permanent manner on the inside of the spool and on an inspection document attached to the spool covering in accordance with MIL-STD-130 with the following information.

    a.   Supplier's name and material designation.

    b.   Part number (see 6.4).

    c.   Lot number (see 4.2.2).

3.4 **Workmanship.** Workmanship shall be such that the reinforcement is free from tears, holes, impurities, non-uniform width and thickness, and other defects which would render the reinforcement unsuitable for the intended purpose.

4.0 QUALITY ASSURANCE PROVISIONS

4.1 **Responsibility for inspection.** Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection requirements specified herein. Except as otherwise specified, the supplier may utilize his own facilities or any commercial laboratory acceptable to the procuring activity. The procuring activity reserves the right to perform any of the inspections or tests set forth in the specification where such inspections are deemed necessary to assure supplies and services conform to prescribed requirements.

4.2 **Quality conformance inspection.** Quality conformance inspection shall consist of the examinations and tests specified in table II.

Table II. Quality Conformance Inspections and Tests

Test or inspection	Requirement	Test method
Visual examination	3.3, 3.4 and section 5	4.3.1
Carbon assay	3.2.1	4.3.2
Moisture content	3.2.1	4.3.2
Ash content	3.2.1	4.3.3
Weight	3.2.1	4.3.4
Breaking strength	3.2.1	4.3.5
Specific gravity	3.2.1	4.3.6
Thickness	3.2.	4.3.7
Certification	3.1	4.3.8

4.2.1 **Sampling.**

4.2.1.1 **Visual examination.** Sampling for visual examination to determine conformance to 3.3 and section 5 shall consist of a random selection of at least 10 percent of the rolls in the lot. Sampling for visual examination to determine conformance to 3.4 shall consist of the samples selected in accordance with 4.2.1.2.

4.2.1.2 _Sample size._ Sampling for tests shall consist of the number of rolls specified in table III, selected at random from each lot. Material shall be selected from the exposed end of the sample roll in sufficient quantity to perform the quality conformance tests.

Table III. Sampling for Tests

Number of rolls in lot	Number of sample rolls to be selected for testing
1 to 3	All
4 to 40	3
41 to 65	4

4.2.2 _Lot._ A lot shall consist of all the reinforcement manufactured at one time using identical processes and materials and submitted for acceptance at one time.

4.3 _Test methods._

NOTE

Reagent grade chemicals shall be used for chemical reactions in the conduct of all tests defined in this specification. Solvents and indicators may be commercial nonreagent grade materials.

4.3.1 _Visual examination._ Samples selected in accordance with 4.2.1.1 shall be visually examined to determined compliance with 3.3, 3.4 and section 5. Unless otherwise specified, all visual examinations shall be conducted with an unaided eye, except for normal corrected vision.

4.3.2 _Carbon assay and moisture content._ Carbon assay and moisture content shall be determined in accordance with the following:

a.   Weigh the specimen to the nearest 0.1 milligram (mg).

b.   Dry the specimen to a constant weight at 225 plus or minus 5 degrees F. Determine the weight of the dried specimen to the nearest 0.1 mg.

c.   Determine carbon assay in accordance with ASTM D 3176. Calculate the percent carbon to the nearest 0.1 percent based on the weight of the dried specimen.

d. Calculate the moisture content to the nearest 0.10 percent in accordance with the following.

$$\text{Percent moisture} = \frac{W_1 - W_2}{W_1} \times 100$$

Where: W_1 = weight of specimen prior to drying, grams (g)

W_2 = weight of specimen after drying, g

e. Report the carbon assay and moisture content as the average of a minimum of three determinations.

4.3.3 **Ash content.** Ash content shall be determined in accordance with the following:

a. Dry approximately 3 g of carbon reinforcement in an air circulating oven at 225 plus or minus 5 degrees F for not less than one hour.

b. Remove the specimen, place in desiccator, and cool to ambient temperature.

c. Weigh approximately 2 g of the cooled specimen into a tared crucible and place into a muffle furnace at 1400 plus or minus 25 degrees F for not less than 3 hours. The weights of the specimen and crucible shall be measured to the nearest 0.001 g.

d. Raise furnace temperature at end of three hours to 1600 degrees F plus or minus 25 degrees F for not less than one hour.

e. Allow an additional 30 minutes burning time or until a constant weight is obtained should ashing be incomplete.

f. Remove specimen and crucible and place them in desiccator.

g. Obtain the post-heat weight of specimen and crucible to the nearest 0.001 g and calculate the percent ash as follows:

$$\text{Precent ash} = \frac{A - B}{W} \times 100$$

Where: A = weight of crucible and ash, g

B = weight of crucible, g

W = weight of specimen, g

h. Report ash content as the average of a minimum of three determinations to the nearest 0.10 percent.

4.3.4 <u>Weight.</u> Weight of the reinforcement shall be determined in accordance with ASTM D 3776. Report the average of a minimum of three determinations.

4.3.5 <u>Breaking strength.</u> Breaking strength of the reinforcement shall be determined in both the warp and fill directions in accordance with ASTM D 1682. Report the average of a minimum of three determinations for each direction.

4.3.6 <u>Specific gravity.</u> Specific gravity shall be determined in accordance with ASTM C 135 or ASTM C 604. Report the average of a minimum of three determinations.

4.3.7 <u>Thickness.</u> Thickness of the reinforcement shall be determined in accordance with ASTM D 1777 using a pressure of 5 plus or minus 4 pounds per square inch. Report the average of a minimum of three determinations.

4.3.8 <u>Certification.</u> The supplier shall certify that the reinforcement meets the material requirements specified in 3.1.

5.0 PREPARATION FOR DELIVERY

5.1 <u>Packaging.</u> The carbon fabric reinforcement shall be packaged in accordance with the manufacturer's best commercial practice. Container interior finishes or coatings shall be of such a nature as to prevent contamination of the reinforcement.

5.2 <u>Packing.</u> The carbon fabric reinforcement shall be prepared for shipment in accordance with commercial practice to insure carrier acceptance and safe transportation at the lowest rate to the point of delivery and shall meet, as a minimum, the requirements of carrier rules and regulations applicable to the mode of transportation.

5.3 <u>Marking for shipment.</u> Each shipping container shall be marked in a permanent manner in accordance with MIL-STD-129 and shall include, but not be limited to, the following:

    a.   Part number (see 6.4) and revision of this specification.

    b.   Supplier's name and material designation.

    c.   Lot number (see 4.2.2).

    d.   Number of rolls of tape and net weight of rolls.

5.3.1 <u>Shipping document.</u> A shipping document which shall be attached to a container per each shipment shall include, but not be limited to:

    a.   Part number (see 6.4) and revision level.

    b.   Date of shipment.

    c.   Contract or purchase order number.

    d.   Date of manufacture.

4.2 Quality conformance inspections. Each nozzle component specified herein shall be subjected to the examinations and tests specified in table IV. Acceptance at the next assembly shall be permissible if the inspection technique is capable of detecting the maximum permissible condition and if permission is granted by the procuring activity.

<div align="center">Table IV. Quality Conformance Inspection</div>

Inspections	Requirement Paragraph	Inspection Paragraph
Visual examinations	3.2.2, 3.3, and section 5	4.3.1
Nondestructive inspection	3.2.4	4.3.2
Compressive strength	3.2.1	4.3.3
Specific gravity	3.2.1	4.3.4
Resin content (carbon, graphite and PAN)	3.2.1	4.3.5
Resin content (silica)	3.2.1	4.3.6
Volatiles content	3.2.1	4.3.7
Flexural strength	3.2.1	4.3.9
Weight	3.2.2	4.3.10
Leak check	3.2.5	4.3.11

4.3 Inspection methods.

4.3.1 Visual examination. Each nozzle component shall be visually examined to determine compliance with 3.2.2, 3.3, and section 5. All phenolic parts shall be examined using alcohol on machined surfaces as an aid for inspecting for cracks and delaminations. Cork shall be visually inspected and verified by touch to determine if a pocket exists between the cork and the aft exit cone overwrap.

4.3.2 Nondestructive inspection. Each nozzle component shall be nondestructively inspected to determine compliance with 3.2.4. Determination of anomaly size may be augmented by nondestructive inspection methods as defined on the drawing. Distance between plies also may be determined by a surface measurement if a tangential radiograph confirms that the ply separation has constant thickness within 25 percent or is a maximum on the surface.

4.3.3 Compression strength. Compression strength shall be determined in accordance with ASTM D 695 and the following:

    a.   Test samples shall be in accordance with ASTM D 695, section 6.7.1.

    b.   Using a load rate of 0.05 inch per minute, load the sample to failure.

    c.   Report the compressive strength for each sample. The average of three determinations shall meet the requirements of table I.

4.3.4 Specific gravity. Specific gravity shall be determined in accordance with ASTM D 792. Report three determinations. The arithmetic mean of the three determinations shall conform to 3.2.1.

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8-10

4.3.5 <u>Resin content for carbon, graphite, and PAN.</u> Resin content for carbon, graphite, and PAN components shall be determined in accordance with the following:

a. Set up the apparatus as shown in figure 6.

b. Devolatilize a sample, consisting of 3 to 10 grams (g) of chips or a piece approximately 0.5 by 0.25 by 1 inch, by conditioning it in a circulating-air oven at 325 plus or minus 5 degrees Fahrenheit (F) for a minimum of 20 minutes, then cooling it in a desiccator to room temperature.

c. Weigh the sample to the nearest 0.001 g.

d. Affix a Vycor test tube containing the sample to the side arm of the vacuum flask. All joints shall be airtight.

e. Start the vacuum pump, evacuate the system, and check for air leaks by clamping off the hose to the vacuum pump. The leak rate shall be less than 0.005 millimeter (mm) per minute as measured with the manometer.

f. With the vacuum pump running and manometer pressure stabilized, place Fisher burners under the sample so that the flame area covers the sample completely.

NOTE

A tube furnace maintained at 1,500 plus or minus
25 degrees F may be used in place of the Fisher
burners.

g. During pyrolysis, some residue may collect at the top of the Vycor test tube (proximal to the vacuum flask). Should this happen, apply heat to the area until the residue has dissipated.

h. Continue pyrolysis for a minimum of 30 minutes, or until the manometer reading is the same as before pyrolysis, whichever is longer.

i. When pyrolysis is complete, turn off the burners and allow the sample to cool under vacuum to room temperature.

j. When the sample is cool, turn off the vacuum pump and carefully remove the vacuum hose from the open arm of the manometer, thus allowing atmospheric air to fill the system and restore pressure equilibrium.

k. Remove the Vycor test tube from the vacuum flask, and wipe any residue from the top of the test tube with a clean, lint-free cloth.

l. Immediately weigh the sample to the nearest 0.001 g.

m. Calculate the dry resin content as follows:

$$\text{Dry resin, percent} = (1.00 - W_2/W_1)\ 100\ (K)$$

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Where: W_2 = weight of sample after pyrolysis, g

W_1 = weight of sample before pyrolysis, g

K = value as defined in material procuring specification

n. Report no less than three determinations. The arithmetic mean shall conform to 3.2.1.

4.3.6 <u>Resin content for silica.</u> Resin content for the silica components shall be determined in accordance with the following:

a. Weigh 5.5 plus or minus 0.5 g of sample (or a piece 0.5 by 0.25 by 1 inch) to the nearest 0.001 g into a previously fired (1,450 degrees F) and tared crucible.

b. Devolatilize the sample by conditioning the sample and crucible in a circulating-air oven at 325 plus or minus 10 degrees F for not less than 20 minutes, then cool in a desiccator and reweigh to the nearest 0.001 g to obtain the sample weight. Designate this weight as W_1.

c. Place the sample and crucible in a muffle furnace.

d. Condition the sample at 1,450 plus or minus 10 degrees F for not less than 3 hours.

e. Cool the sample in a desiccator to room temperature, and reweigh to the nearest 0.001 g to obtain the final sample weight. Designate this weight as W_2.

f. Calculate the resin content as follows:

$$\text{Resin solids, percent} = \frac{W_1 - W_2}{W_1} \times 100$$

Where: W_1 = sample weight after volatile removal, g

W_2 = sample weight after volatile removal and 3 hours minimum at 1,450 plus or minus 10 degrees F, g.

g. Report not less than three determinations. The arithmetic mean shall conform to 3.2.1.

4.3.7 <u>Volatiles content.</u> Volatiles content shall be determined in accordance with the following:

a. Cut a sample measuring 2 inches by 0.5 inch by 0.25 inch plus or minus 0.125 inch. Wipe the sample clean and allow it to air dry for not less than 20 minutes before testing.

b. Place the sample in a desiccator and dry for not less than 45 hours nor more than 51 hours.

c. Weigh the sample to the nearest 0.01 g and record as W_1.

d. Place the sample in a circulating-air oven that has been preheated and stabilized at 325 plus or minus 10 degrees F for not less than 30 minutes. Condition the sample at 325 plus or minus 10 degrees F for 4 to 4-1/2 hours or 118 to 122 hours as specified in table I. For samples to be conditioned for greater than 4-1/2 hours include the out time required below.

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e. Remove the sample from the oven and cool in a desiccator for approximately 30 minutes or until the sample reaches room temperature. For samples to be conditioned for greater than 4-1/2 hours remove the samples at 4-1/2 hours, 24 hours, 48 hours, 72 hours, 96 hours, and 118 hours. The total time outside the circulating-air oven shall not exceed 6 hours prior to reaching the 118 hour requirement in step d.

f. Reweigh the sample after each time designated above and report the value to the nearest 0.01 g along with the date and time of each measurement. Record the final measurement per table 1 as W_2. The removal, weighing, and recording steps at 24 hours, 48 hours, 72 hours, and/or 96 hours may be bypassed when they occur on weekends or holidays.

g. Calculate the percent of residual volatiles as follows:

$$\text{Volatiles, percent} = \frac{W_1 - W_2}{W_1} \times 100$$

Where: W_1 = original weight of sample, g

W_2 = weight of sample after heating, g.

h. Report not less than three determinations. The arithmetic mean shall conform to 3.2.1.
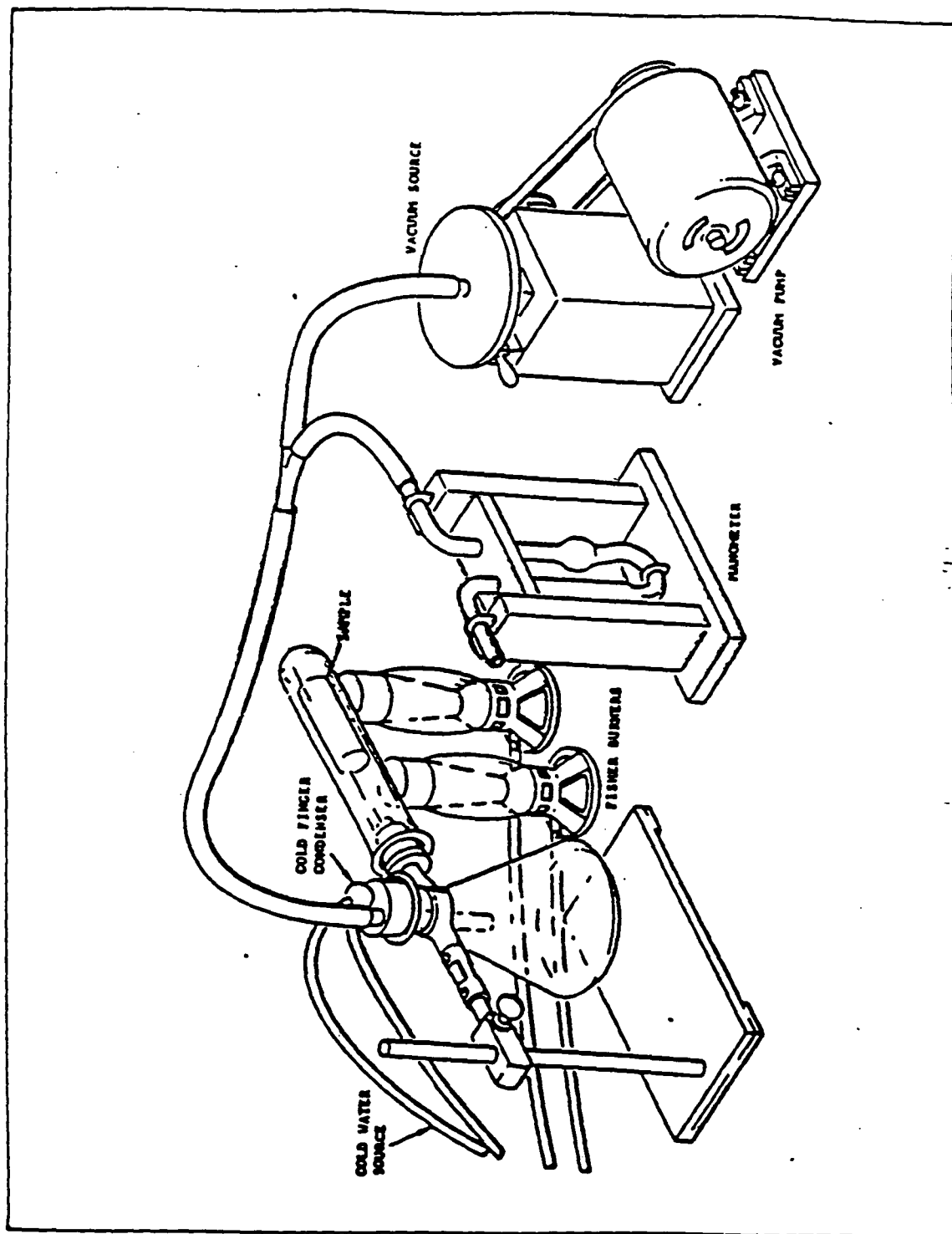
4.3.8 Deleted.

4.3.9 Flexural strength. Flexural strength shall be determined in accordance with ASTM D 790, method 1, under the following conditions.

a. Test samples shall have a minimum length of 4 inches. The span-depth ratio shall be a minimum of 10.

b. The contact edge of the loading nose and two end supports shall be rounded to a minimum radius of .1/8 inch.

c. Wipe the sample with isopropyl alcohol. No crack indications shall be permitted.

d. Record the sample depth and width to an accuracy of plus or minus 0.001 inch.

e. Mark the center of sample to an accuracy of plus or minus 0.030 inch.

f. Load the sample with loading nose at marked center. The rate of head travel shall be 0.2 to 0.25 inch per minute.

g. Distance between supports of the test fixture shall be 3.000 plus or minus 0.010 inch.

h. Report the flexural strength for each sample. The average of three determinations shall meet the requirement of table 1.

4.3.10 Weight. Each deliverable component/assembly shall be weighed with an instrument accurate to within plus or minus 1 percent.

4.3.11 Leak check. Each O-ring joint of each nozzle assembly shall be leak checked to determine compliance with 3.2.5 as follows:

14.

VACUUM SOURCE

VACUUM PUMP

SAMPLE

COLD FINGER CONDENSER

COLD WATER SOURCE

FISHER BURNERS

FLUXOMETER

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GARY BROWN

SPIP - NOZZLE INITIATIVE ADVISORY COMMITTEE ON CARBON PHENOLIC CONSTITUENT AND COMPOSITE TEST METHODOLOGY

12th Biannual Meeting

Mississippi State University
"M" Club Conference Room
Starkville, Mississippi

Thursday, May 19, 1994

2:00 pm - 3:00 pm   Open Forum on Performance Based Acceptance Testing - Industry Experience

Gary Brown, Aerojet

Propulsion Systems Plant

GenCorp
AEROJET

AEROJET PEACEKEEPER MOTOR
2ND STAGE

TAG END TEST DATA

VERSUS

FIRED EXIT CONE LINER PERFORMANCE

STD DENSITY CCP

LOW DENSITY CCP
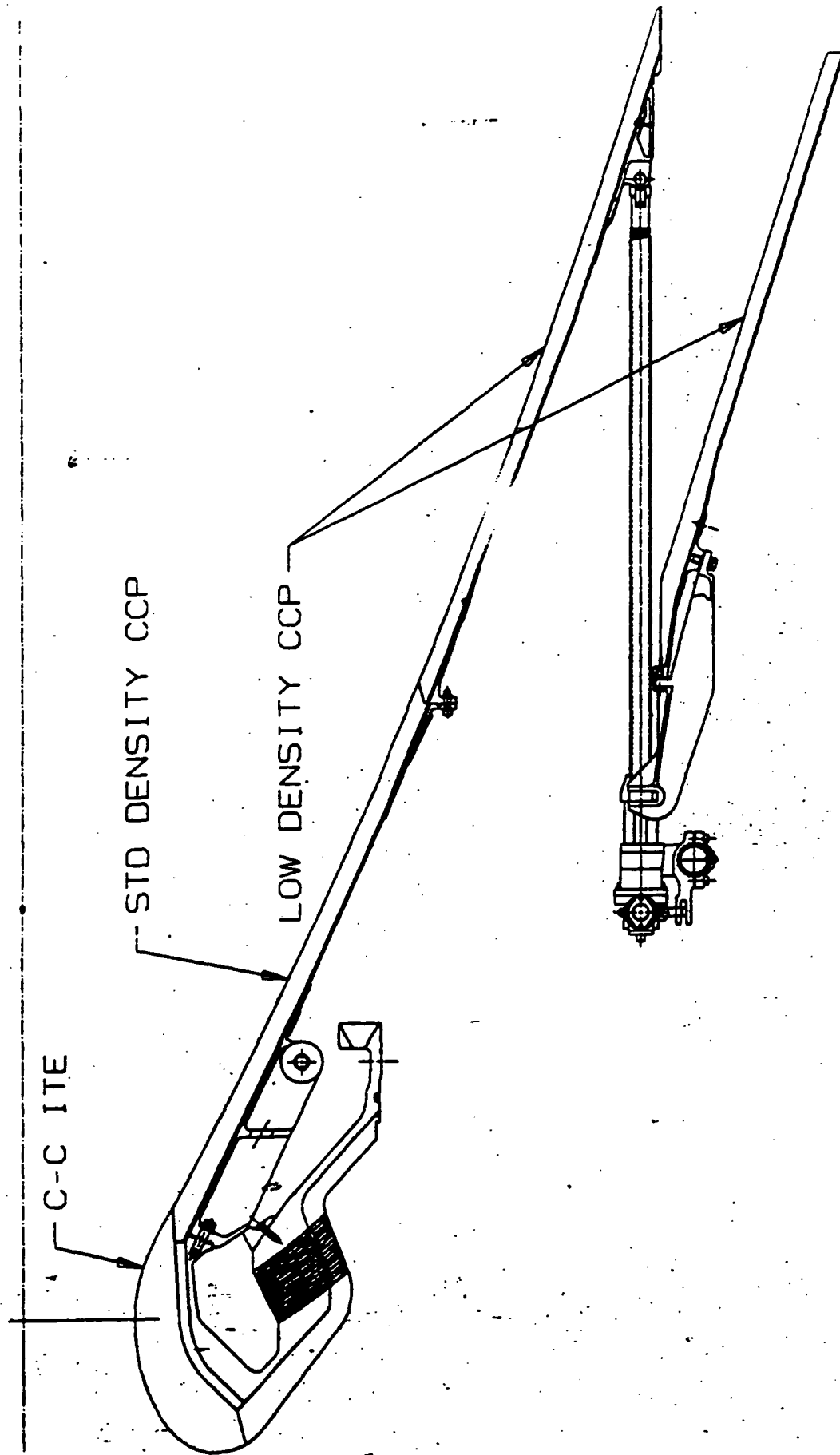
C-C ITE

Figure 2,α-1 Stage II Peacekeeper Nozzle Design

CARBON PHENOLIC/LOW DENSITY EXIT CONES

MATERIAL PROPERTIES VERSUS MOTOR PERFORMANCE

MOTOR I.D.	MATERIAL MANUF.	FILLER CONT %/WT	S.G. CURED LAM	AVG COMP STR-LAM (K)	AVG COMP STR ENECS (K)	RESIDUAL VOLS ENECS	SPALLING	SECONDS SPALLATION TIME
DS-8A	F	NA			16.5	0.37	YES	42
	NA	NA			22.0	1.33	NO	58
PT-2	P	NA	0.983		15.5	0.60		
	P	7.6			11.7	0.43	NO	
PT-4	P	6.9			11.9	0.26	NO	
	F	9.6	1.0	19.4	15.3	1.7	NO	
Q-1	P	9.5	0.99	24.4	13.0	0.63	NO	11
	F	10.2	0.98	19.4	16.1	0.08	YES	41
Q-3	P	8.5	0.99	25.83	25.0	0.42	YES	11
	P	8.5	0.99	27.83	13.4	0.73	NO	13
Q-4	F	12.0	0.99	23.8	14.9	0.24	YES	12
	F	12.1	1.01	25.0	15.8	0.33	YES	19
Q-5	F	12.1	1.01	25.0	14.6	0.29	YES	11
	F	12.1	1.01	25.0	20.9	0.87	YES	23
Q-6	P	8.2	0.96	24.9	12.4	0.47	NO	
	P	8.7	0.97	25.6	12.4	0.42	NO	
Q-7	F	11.7			13.4	0.64	YES	
	F	10.7	1.01	23.5	15.1	0.43	YES	NA
Q-8	F	11.4	1.02	23.8	13.2	0.84	YES	12
	F	11.8	1.03	19.3	14.6	0.57	YES	32
Q-1A	P	8.2	1.01	29.40	12.6	0.60	NO	
	P	8.0	1.01	29.40	14.8	0.74	NO	
F-10A	F	12.0			15.7	1.64	FLIGHT DATA INDICATIONS	
	F	12.0			14.3	0.37	FLIGHT DATA INDICATIONS	
F-11	F	12.0			15.7	1.64	FLIGHT DATA INDICATIONS	
	P	8.2			16.5	0.97	FLIGHT DATA INDICATIONS	
F-12	F	12.1			15.8	0.10	FLIGHT DATA INDICATIONS	
	P	8.4	0.96	24.9	12.5	1.13	FLIGHT DATA INDICATIONS	
F-13	F	11.8			18.6	0.64	FLIGHT DATA INDICATIONS	
	F	11.8	1.01	20.4	13.4	2.08	FLIGHT DATA INDICATIONS	
F-14	F	11.4	1.01	20.4	15.6	0.47	FLIGHT DATA INDICATIONS	
	F	11.7	0.98	18.5	13.9	0.62	FLIGHT DATA INDICATIONS	
F-15	F	11.3	1.01	22.0	14.7	0.71	NO	
	F	11.9	1.03	18.8	14.1	0.52	NO	
+15 ADDITIONAL MOTORS							NO	
							NO	

F - FIBERITE

P - POLYMETRIC

NA - NOT AVAILABLE

	PROPERTY	UNIT	MIN	MAX
A.	RESIN SOLID CONTENT	WT/%	34.0	42.0
B.	FILLER CONTENT	WT/%	5.0	13.0
C.	SPECIFIC GRAVITY	GMS/CC	0.95	1.05
D.	RESIDUAL VOLATILES	WT/%	---	2.50
E.	COMPRESIVE STRENGTH IN WRAP DIRECTION	LEF/IN2	18,000	--

GenCorp
AEROJET

Propulsion Systems Plant

TAG END TEST DATA SUMMARY

		COMMENT
SPECIFIC GRAVITY RANGE	0.96 - 1.03 GM/CC	NO APPARENT CORRELATION
COMPRESSION STRENGTH RANGE	11.7 - 25.0 KSI	NO APPARENT CORRELATION
RESIDUAL VOLATILES	0.08 - 2.08%	NO APPARENT CORRELATION
MICROBALLOON FILLER	7.6 - 12.1	> 10% SPALLATION < 10% NO SPALLATION

Fig. 2. Microballoon Content Versus Composite Density—Low-Density Carbon Phenolic

FILLER CONTENT MINIMUM/MAXIMUM

%/WEIGHT/INDIVIDUAL ROLLS IN ENECS

FILLER CONTENT %/WT.

FIBERITE-EXTENSION
FIBERITE-TRANSLATING
POLYMERIC-EXTENSION
POLYMERIC-TRANSLATING

FPT-2 FPT-4 PQ-1 PQ-3 Q-4 Q-5 Q-6 Q-7 Q-8 Q-1A FTM-10A FTM-11 FTM-12 FTM-13 FTM-14

LDC SPALLATION/PLY LIFT (PL)

DS/8A THROUGH FTM-16

(18 MOTORS - 36 LDC CONES)

EXTENSION CONES

11 KAISER
- 8 FIBERITE (ALL SPALLED PLY LIFT)
- 3 POLYMERIC (NO SPALLING)

8 AEROJET
- 4 FIBERITE (ALL SPALLED PLY LIFT)
- 3 POLYMERIC (1 SPALLED)

TOTAL 5055 LDC

POLYMERIC - 13 CONES THROUGH FTM-16
12 CONES - NO SPALLING/NO PLY LIFT
1 CONE SPALLED/NO PLY LIFT

TRANSLATING CONES

2 HAVEG
- 1 FIBERITE (NO SPALLING)
- 1 POLYMERIC)NO SPALLING)

8 KAISER
- 5 FIBERITE (ALL SPALLED PLY LIFT)
- 3 POLYMERIC (2 NO - A FLT DATA)

6 AEROJET
- 3 FIBERITE (2 SPALLED PLY LIFT - 1 FLT DATA)
- 3 POLYMERIC (2 NO SPALLING - 1 FLT DATA)

TOTAL 4926 LDC

FIBERITE 21 CONES THROUGH FTM-16
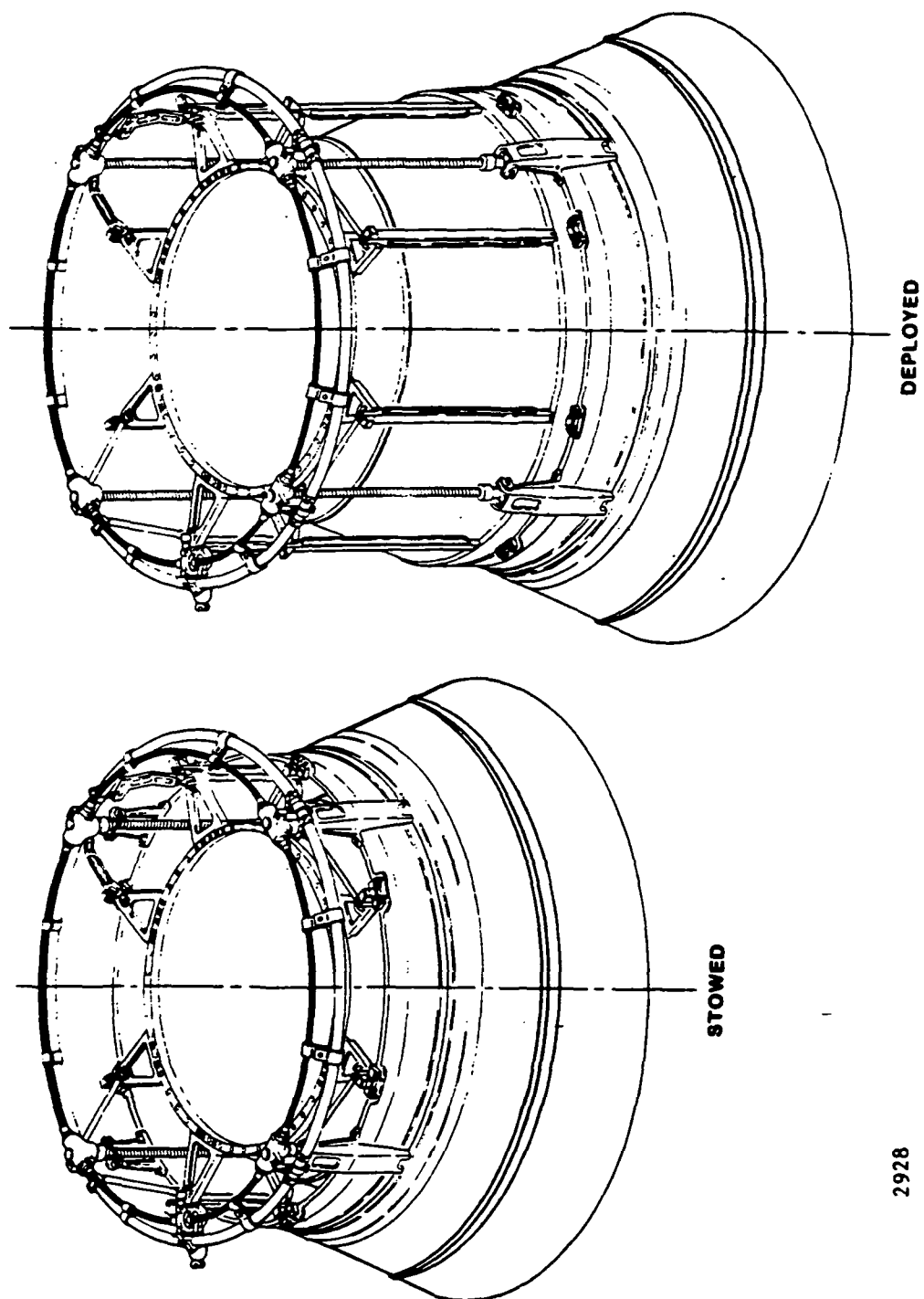20 CONES SPALLED AND PLY LIFT
1 CONE - NO SPALLING/PLY LIFT - FILLER CONTENT - 9.6%

DEPLOYED

STOWED

2928

Figure 3.2.6-1.   ENEC Assembly